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MSAR 71-122

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INTERIM REPORT

to

National Air Pollution Control Administration
Consumer Protection and Environmental Health Service
U. S. Department of Health, Education and Welfare
Durham, North Carolina 27701

Contract No. PH 22-68-11
MSAR Job No. XA 720451

INORGANIC LIQUIDS FOR REMOVING SO_2 FROM FLUE GASES

PHASE II

July 1971

MSA RESEARCH CORPORATION
Evans City, Pennsylvania

and

SINGMASTER & BREYER
New York, N. Y.

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16. Abstracts

A laboratory investigation has been made on those candidate Systems for SO_2 removal that were developed during a literature search in Phase I of this project. Emphasis in this investigation was placed on the definition of those parameters which would allow a more definitive engineering evaluation. Of the four candidate systems recommended in Phase I, the non-regenerable limestone-molten nitrate system, and the adduct or complex-forming molten nitrate system have been rejected. The remaining candidate systems - the molten nitrate-calcium oxide system and the tin-lead alloy system-have been investigated in some detail. Comparison studies of the various reactive oxides dissolved or suspended in the molten nitrate solvents have shown that the best reactant is calcium oxide. The complete results of this experimental program are presented in the report.

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FOREWORD

This report summarizes the studies performed under Phase II of Contract PH 22-68-11 on "The Applicability of Inorganic Liquids for Removing SO_2 From Flue Gases". This Phase II study was a laboratory investigation of concepts developed during the Phase I literature survey and preliminary engineering evaluation. The interim report covering Phase I studies was published April 9, 1969.

The studies covered in this Phase II interim report were conducted during the period January 20, 1969 through May 31, 1970. The investigations were performed by MSA Research Corporation of Evans City, Pennsylvania and Singmaster and Breyer (a partnership) of New York, New York. Contributing personnel were Frederick Tepper (project director through August 1969), William J. Cooper (project director from August 1969 to completion) and John S. Greer of MSA Research Corporation and Elliott Goldberg, Don Lee Stockton, Faustino Prado, William Prosk and Stefan Daniec of Singmaster and Breyer. The Project Officer is Mr. E. D. Margolin, Control Technology Research and Development Programs, National Air Pollution Control Administration, Public Health Service, Cincinnati, Ohio.

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INTERIM REPORT
on
INORGANIC LIQUIDS FOR REMOVING SO_2 FROM FLUE GASES
PHASE II

SUMMARY AND CONCLUSIONS

A laboratory investigation has been made on those candidate systems for SO_2 removal that were developed in the Phase I literature survey. Emphasis in this investigation was placed on the definition of those parameters which would allow a more definitive engineering evaluation.

Of the four candidate systems recommended in Phase I, two have been rejected from consideration for further study. The non-regenerable limestone-molten nitrate systems has been discarded because of the consideration that "dead-end" processes are not of interest at this time. The adduct or complex-forming molten nitrate system has been rejected after a brief experimental study showed that the predicted performance could not be achieved in actual tests.

The remaining candidate systems - the molten nitrate-calcium oxide system and the tin-lead alloy system - have been investigated in some detail.

Comparison studies of the various reactive oxides dissolved or suspended in the molten nitrate solvents have shown that the best reactant is calcium oxide. Other oxides are not sufficiently basic, from a Lux-Flood acid-base standpoint, to absorb SO_2 efficiently and, at the same time, minimize undesirable side reaction with the nitrate solvent.

Absorption rate studies of the CaO-molten nitrate system have shown that, under stagnant or slow surface-renewal conditions, the rate of absorption is comparable to that of SO_2 or CO_2 into basic aqueous solutions. Experimental results indicate that the rate controlling step in the absorption of SO_2 from simulated stack gases is diffusion in the liquid phase. Thus a gas-liquid contactor which provides a high rate of surface renewal should allow rapid, efficient SO_2 absorption.

The reaction products of the absorption of SO_2 by the CaO-nitrate system, $CaSO_3$ and $CaSO_4$, can be concentrated by centrifugation and separated as an insoluble fraction by water washing. Reductive regeneration by a carbon reductant (coal or coke) can yield either SO_2 directly at high temperatures, or, at somewhat lower temperatures, CaS which can be treated with steam and CO_2 to yield H_2S as the S-containing product.

The tin-lead alloy system has been found to undergo severe oxidation in the presence of the excess air in the flue gases. Oxidation can be minimized without seriously affecting SO_2 absorption by the addition of about 0.5 weight percent Zn to the Sn-Pb eutectic. Experimental difficulties in maintaining a completely molten system hindered absorption studies at high surface agitation conditions, but the data obtained indicate satisfactory absorption could be achieved in an agitated pool type of reactor such as that used in the Imperial Smelting Process for zinc condensation.

The reaction products of SO_2 absorption by the Sn-Pb-Zn system are primarily sulfides and oxides of Sn and Zn. These products form a dross which can be mechanically removed from the surface of the molten metal and transferred to a reductive regeneration system. Standard metallurgical practices can be used to reduce the sulfides and oxides to yield SO_2 and the regenerated metal.

Investigation of NO_x absorption showed that only slight NO_x absorption can be expected under efficient SO_2 absorption conditions, for both the CaO-nitrate and the molten metal systems.

Screening studies of potential modifications to the concept of inorganic liquids for SO_2 absorption, such as the use of phosphates or the "in-situ" formation of reactive oxides, have not shown sufficient promise to justify engineering evaluation.

Literature data on the physical properties of the molten nitrate system have been compiled and supplemented by a few experimental measurements.

Experimental corrosion studies of Armco iron and mild steel in the molten nitrate solvent have shown that mild, low-carbon steel can be satisfactorily used for containment and construction. Negligible attack occurred with no apparent effects at the gas-liquid interface.

INTRODUCTION AND BACKGROUND

During 1968, a literature survey was performed to determine the applicability of inorganic liquids in new processes for removing SO_2 from stack gases. The survey included the analysis of solubility and phase data for inorganic compounds and estimates of their thermal and chemical reactivity under stack gas conditions. Estimations were made on the basis of thermodynamic and physical data to aid in the development of hypothetical processes for inorganic liquid SO_2-scrubbing systems.

Four candidate schemes were developed for preliminary engineering and economic evaluation. The candidates included one liquid metal and three molten salt schemes.

The liquid metal scheme involved the use of lead-tin eutectic as the reactive stack gas scrubber. Removal of SO_2 by reaction with the metal components would be followed by separation of the sulfide-oxide dross for carbothermic reduction to regenerate the metals.

Several alternatives were possible with the molten salt schemes. One process would involve the absorption of SO_2 by limestone, dissolved in a molten nitrate eutectic, to form $CaSO_x$. The sulfur-containing products of this reaction would be filtered and discarded with other plant wastes, such as fly ash.

A "closed cycle" modification of this scheme would use CaO, dissolved in the nitrate eutectic, as the reactive sorbent. The sulfur-containing products from this reaction would be removed to a separate regeneration system, where CaO would be thermochemically regenerated.

The third molten salt scheme involved the use of adduct-forming compounds in molten salt system to remove SO_2. A candidate system, such as $MgSO_4$ in the urea-KNO_3-$NaNO_3$, eutectic, would absorb SO_2 by complex formation for subsequent removal by steam or inert gas stripping.

Based on the findings of the Phase I program, an experimental program, Phase II, was conducted to define and measure those factors necessary for a more refined evaluation of the candidate processes. The results of the Phase II experimental program are presented in this report.

Intentionally Blank

DESCRIPTION OF CANDIDATE SCHEMES

A more detailed outline of candidate inorganic liquid schemes is possible by combining data from the literature survey with that of the experimental program. Compiling these data for this interim report provides a basis for more rigorous correlations and economic evaluation of the candidate schemes.

Proposed Molten Metal Scheme

The postulated molten metal scheme would utilize a ternary alloy containing tin, lead and zinc as the absorbing medium. An alloy containing approximately 65.3 weight percent Sn-34.2 weight percent Pb-0.5 weight percent Zn would provide adequate absorption with minimum deterioration.

Absorption in the liquid metal contactors has been sensitive to surface area and exposure times. The absorption reaction is fairly complex, with the overall reaction being a composite of several oxidation and replacement reactions:

$$\mathrm{Sn,Pb,Zn} + \mathrm{SO_2} \longrightarrow \mathrm{Sn,ZnS} + 2\mathrm{Sn,Pb,ZnO}.$$

SO_2 absorption is nearly eliminated by the addition of other oxidation suppressors, such as aluminum. The reaction with SO_2 apparently occurs after an initial, partial oxidation. The postulated reaction:

$$\mathrm{Sn,Pb,Zn} + \mathrm{O_2} \longrightarrow \mathrm{Sn,Pb,ZnSO_4}$$

might be better represented, mechanistically, by:

$$\mathrm{Sn,Pb,ZnO} + \mathrm{SO_2} + 1/2\ \mathrm{O_2} \longrightarrow \mathrm{Sn,Pb,ZnSO_4}.$$

The initial formation of $SO_x^=$ compounds is followed by a reduction reaction in the alloy matrix:

$$4\mathrm{Sn,Pb,Zn} + \mathrm{Sn,Pb,ZnSO_4} \longrightarrow \mathrm{Sn,ZnS} + 4\mathrm{Sn,Pb,ZnO}.$$

The zinc concentration in the alloy is used to limit oxidation of the alloy during exposure to the stack gases. The 0.5 weight percent concentration has been found to be the best compromise for inhibiting excess oxidation yet not interfering with SO_2 absorption. Zinc concentrations greater than 0.5 weight percent must be avoided in stirred reactors because of phase separation and the formation of PbZn intermetallics.

Sulfide-oxide absorption products remain on the surface of the melt as a dross, which can be scraped from the surface and transferred to a separate regeneration unit. Constitution of this dross depends upon the nature of the alloy, stack gas SO_2 and O_2 concentrations, and contactor parameters. When the oxygen concentration of the stack gas is low (minimum excess air) and rapid, efficient contact occurs between gas and molten metal, tin and zinc sulfide are the predominant products. The oxide (Sn and Zn) concentration is approximately equal to the sulfur concentration and a small amount of sulfite or sulfate has been found. Tin sulfide is the predominant sulfur-containing species and zinc oxide is the predominant oxygen-containing species. The formation of Sn(IV) compounds has been completely eliminated by the use of the zinc ternary alloy.

As the oxygen concentration of the stack gas increases, oxidation exceeds SO_2 absorption. This is no problem in normal operations ($\approx$5 percent O_2), but was found to increase problems with freezing, stratification and absorption when the oxygen concentration was approximately 20 percent.

Regeneration of the metals would be accomplished by a carbothermic reduction after mixing the dross with coal. The dross would consist of a mixture of sulfides, oxides and adhering metals. Non-metallic concentration in the dross has been approximately 35-40 percent in experimental tests.

This mixture would be transferred to a kiln or electric furnace for reduction and regeneration. Carbothermic reduction would be done at approximately 1500°F. Complete reduction of the entire charge to metals would not be necessary since the oxide solubilities are approximately 0.5 weight percent and they have been shown to have a desirable effect on absorption.

Proposed Fused Salt Schemes

The postulated molten salt scheme would utilize an alkali nitrate eutectic (either potassium-lithium or potassium-sodium-lithium) as a solvent for between 2 and 5 weight percent loading of either calcium oxide or carbonate. This mixture would be exposed to stack gases in a contactor designed to utilize between 25 and 35 percent of the reactive absorbent.

The operating exposure or retention time and extent of reaction would have to be calculated on the basis of both stack gas and fly ash sulfur concentrations. It has been assumed for these postulated schemes that there is no fly ash removal prior to the molten salt contactor. The fly ash has no effect on the fused salt mixture except that its sulfur concentration is nearly quantitatively removed and the amount of the reactive absorbent necessary to remove 95 percent of the SO_2 content from the stack gas is increased.

The products from this absorption reaction would be a mixture of sulfate, sulfite and carbonate. If the system is designed to maximize absorption of SO_2 and the reaction is limited to between 25 and 35 percent of the oxide-carbonate loading, the carbonate concentration would be approximately twice that of the sulfur-containing products and sulfite concentration approximately twice the sulfate concentration.

Partial separation of the products would be done in a settling tank by gravity settling. The upper portion of this tank could be recycled after proper oxide or carbonate addition, to the absorption step. Maximum solubility of the sulfated products would be limited to approximately 2 weight percent in the recirculated solvent, which would have little effect except to slightly reduce the maximum solubility of carbonate.

Gravity settling would require long "hold-up" times, which would require excessive eutectic stock for a large installation. Hot centrifuging the "spent" liquid could be used to accelerate product isolation. The concentration of sulfur-containing products has been doubled in experimental tests using a cold centrifuge but, more importantly, the surface concentrations have been reduced to one third of the average, or near the solubility limit. Centrifuging the melt would significantly increase the recycle rate by extracting a portion of the eutectic solvent for immediate recycling.

The concentrated product mixture would be washed with water to remove the remaining nitrate solvent. The insoluble material would be mixed with coal and transferred to a calciner for regeneration. The water from the washings would be evaporated to recover the nitrate salts.

Regeneration would be done in a separate calciner unit at approximately 1500°F. Experimental verifications of the reaction

$$CaSO_4 + C \xrightarrow[1500°F]{\Delta} CaO + SO_2 + CO$$

have been done at lower temperatures, since sulfite is also present. This temperature will assure complete reduction and also the decomposition of carbonate according to

$$CaCO_3 \xrightarrow[1500°F]{\Delta} CaO + CO_2.$$

The SO_2 recovered from either of these schemes would be used to manufacture sulfuric acid.

Alternatively, the reduction could be conducted at somewhat lower temperatures to yield CaS, which can then be treated with steam and CO_2 to give H_2S and $CaCO_3$. Calcination of the carbonate will then yield CaO for recycle.

It is recognized that geographical location, product marketing and raw material availability will require evaluation of optimum regeneration method for specific installations.

APPARATUS AND ANALYTICAL METHODS

The apparatus used in Phase II studies was developed from that used in initial, screening tests by including several improvements where deficiencies had been found. These refinements included:

1) better control and measurement of temperature;

2) means for isolating and analyzing absorption products; and

3) provisions for operating with gas mixtures of several SO_2 concentrations and the simultaneous addition of NO.

A schematic outline of the adsorption apparatus is shown in Figure 1. Simulated stack gas flows could be varied between 50 ml/min and 3 l/min with an accuracy of approximately 3 percent. NO additions, using the micro-flowmeter, could be made between 3 ml/min and 50 ml/min.

Bubbler Contactor

A more detailed sketch of the bubbler is shown in Figure 2. The inner chamber is made of three-inch stainless steel tubing with a micrometallic filter welded to the end. The top and dip tube are also made of stainless steel and a prismatic enclosure of micrometallic filter is welded to the end of the dip tube to aid dispersion of gas flow. The top seal is made through a Teflon gasket.

The fused salt charge was calculated to fill both vessels to a height approximately 1/2 inch above the gas disperser. Tests were usually done at a flow rate of 200 ml/min. Residence time within the melt is calculated at 1.4 seconds.

After exhausting the absorption capacity of the melt, or after the effluent concentration was greater than 1,000 ppm, the molten salt was driven through the micrometallic filter under pure nitrogen pressure. Preliminary results indicated that 75 percent of the salt solvent could be removed in this manner, but later tests, in which the sulfur-containing products were smaller size, removed 60-65 percent. No differences were noted between the filtrations of solvents containing CaO or $CaCO_3$. In all cases the precipitate retained enough of the solvent to form a pasty consistency.

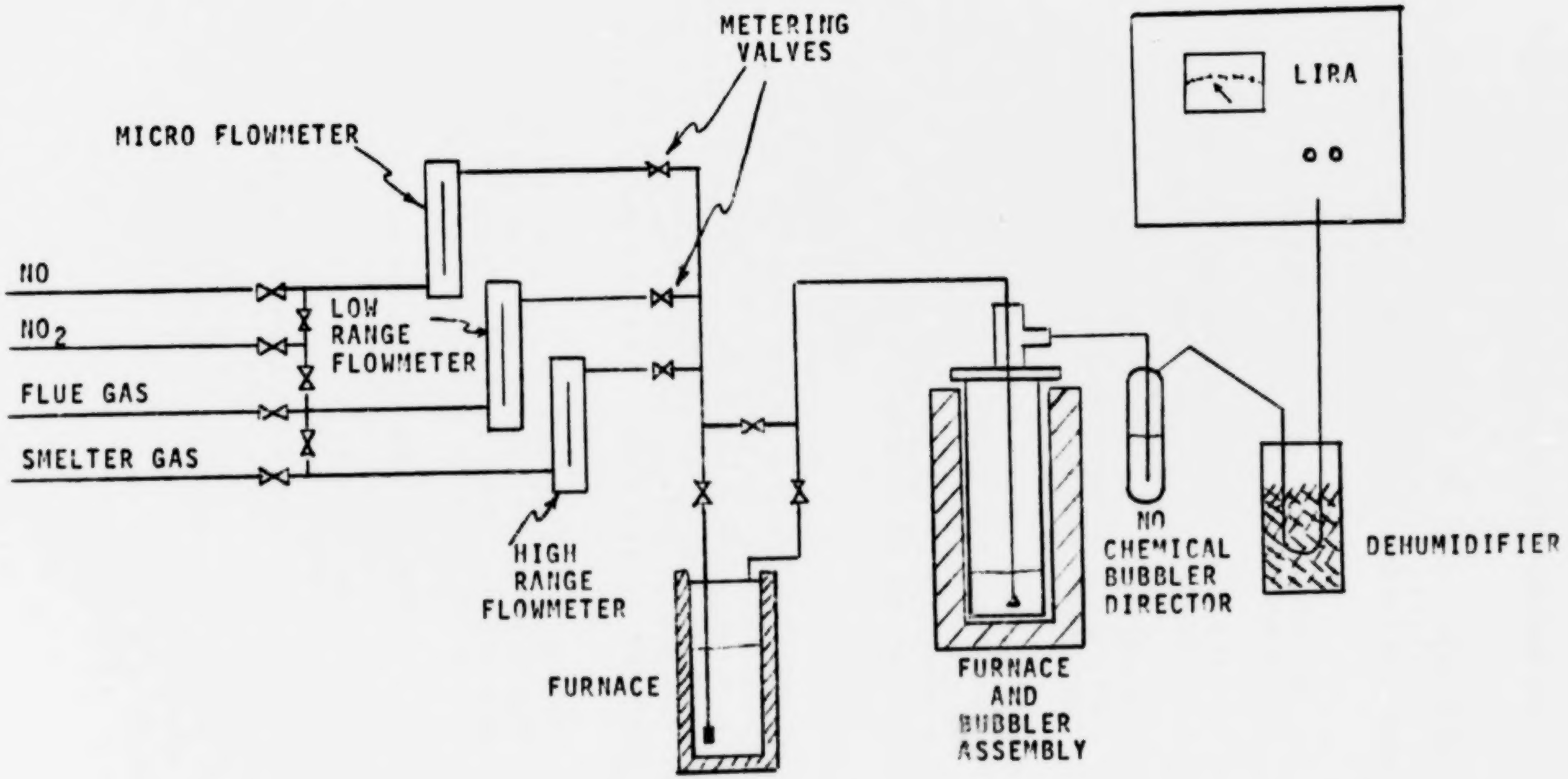
METERING VALVES
MICRO FLOWMETER
LIRA
NO
NO_2
FLUE GAS
SMELTER GAS
LOW RANGE FLOWMETER
HIGH RANGE FLOWMETER
FURNACE
FURNACE AND BUBBLER ASSEMBLY
NO CHEMICAL BUBBLER DIRECTOR
DEHUMIDIFIER

FIGURE 1 - Bubbler and Analysis Train for Phase II Experiments

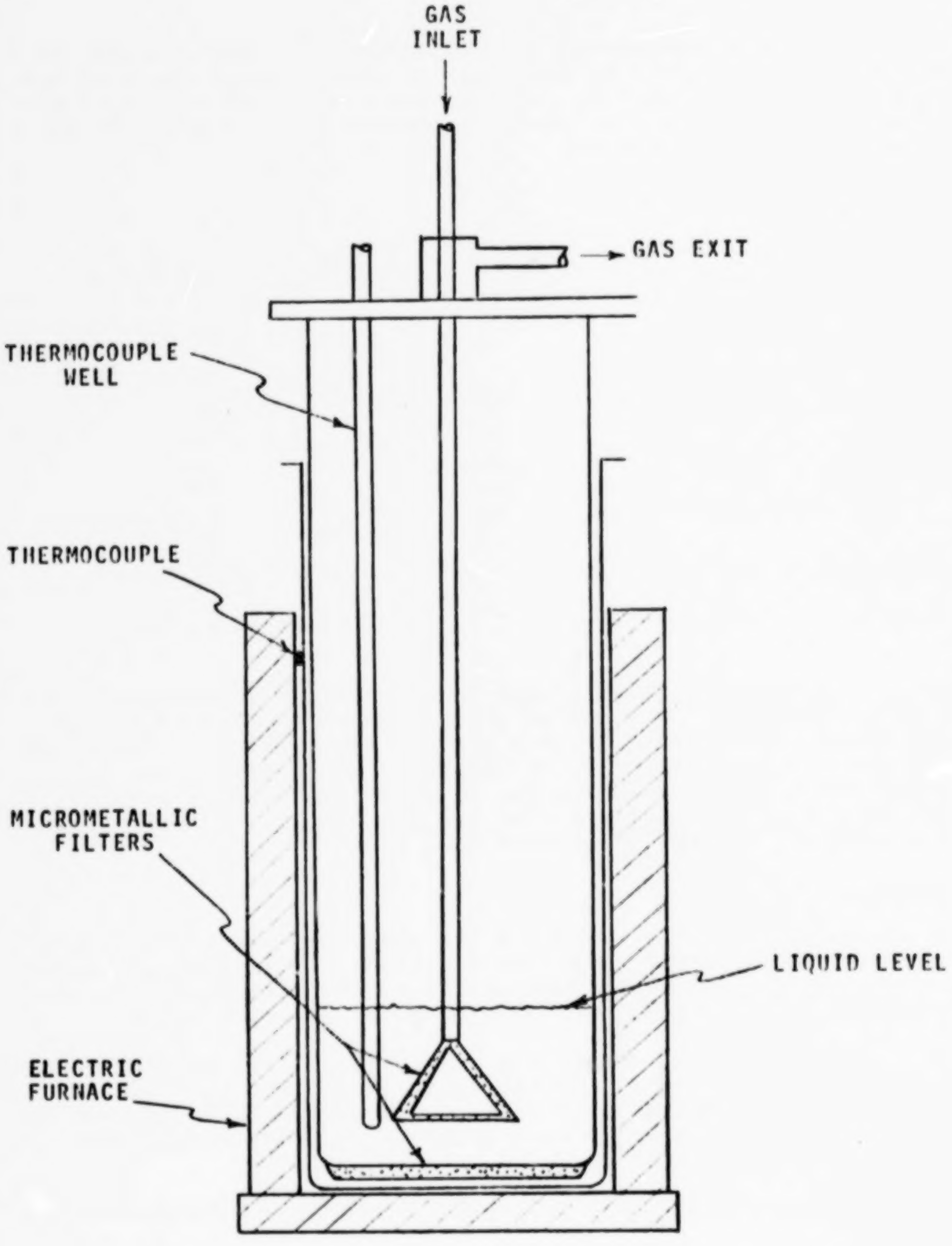
GAS INLET
GAS EXIT
THERMOCOUPLE WELL
THERMOCOUPLE
MICROMETALLIC FILTERS
LIQUID LEVEL
ELECTRIC FURNACE

FIGURE 2 - Bubbler Screening Apparatus

By concentrating the absorption products through filtering, it was easier to characterize the products and possible losses through solubility. These tests indicated that approximately 60 percent of the reactive species charged was reacted un-er these circumstances.

Simulated Stack Gases

Both flue gas (~ 0.3 percent SO_2) and smelter gas (~ 3 percent SO_2) mixtures were obtained from standard gas cylinders. Typical analyses for these gas mixtures are given in Table I.

TABLE I - SIMULATED STACK GAS MIXTURES

% CO_2	% O_2	% N_2	% SO_2	
9.3	6.8	83.5	0.38	Flue gas mixture
15.0	6.1	75.8	3.2	Smelter gas mixture
25.7	13.9	57.6	2.8	Smelter gas mixture

Humidification of the gas mixture was accomplished in a glass bubbler maintained at a temperature to give 10 percent H_2O vapor. Several tests were made on this system to determine its efficiency. Checking the volume of water displaced for a given air flow and weighing the water delivered to a condenser at the end of the delivery line showed that the humidification averaged >95 percent of theoretical.

Analysis

SO_2 concentrations in the simulated stack gases were monitored with an MSA Model 200 SO_2-LIRA. This infrared analyzer is capable of continuously measuring concentrations of SO_2 between 0-1,000 ppm and 0-10,000 ppm on two separate scales.

When corrosion of the measuring cell by SO_x-H_2O mixtures incapacitated the LIRA, several aqueous bubblers were used to follow the SO_x concentration. A standard $KMnO_4$ solution was used for some tests, where the data obtained did not always agree with the assumed reaction:

$$2KMnO_4 + 6SO_2 + 2H_2O \longrightarrow 2KHSO_4 + 2MnSO_4 + H_2S_2O_6.$$

This reaction is both temperature and concentration dependent and efforts were made to obtain the reaction:

$$2KMnO_4 + 5SO_2 + 2H_2O \xrightarrow{[H+]} K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

instead. This latter reaction was more reproducible, but there were some variations noted.

SO_3 concentrations, first noted in the phosphate tests, were measured with an isopropanol bubbler containing 20 percent water. This mixture, followed by a standard I_2 solution, is a standard method for analyzing SO_3 in the presence of SO_2. We found, in these tests with simulated stack gases, that the blank obtained represented a considerable portion of the total SO_x concentration of the stack gas mixture.

Several reagents were studied for continuous monitoring of NO_x concentrations in the effluent gas stream. The reagent of Patty and Patty (1943) was almost too sensitive for operations in the hood area where NO was released, and other colorimetric reagents were also tried in bubbler screening tests. Aqueous solutions of ferrous salts gave adequate color changes at 1,000 ppm concentrations. At these concentrations, the color change resulting when ferrous compounds form coordination compounds with the NO was sufficient to denote its presence.

The Patty and Patty reagent was used in conjunction with the MSA SO_2 LIRA analyzer in tests where NO was added at low concentrations to simulated flue gas. NO was added separately so that its effects could be measured as a function of its relative concentration.

Standard acid-base titrations and barium sulfate precipitation for total sulfur were used with some of the aqueous absorption schemes to follow the deployment of sulfur through these candidate scrubbers. The conclusions obtained from these various analytical manipulations are:

1) that the infrared analyzer provides an adequate method for following SO_2 in the effluent gases of these tests;

2) that a comprehensive knowledge of the reactions occurring in such complex mixtures as these stack gases require the simultaneous use of an assortment of analytical methods for comparison;

3) that data obtained from tests of this type must be scrutinized for synergistic reactions not possible in calibrating mixtures.

Reaction Chemistry

Absorption kinetics were to be obtained from a horizontal tube reactor shown in Figure 3. This contactor was fabricated similar to an apparatus suggested by the subcontractor, Singmaster & Breyer. The horizontal tube reactor is a 12 inch length of nominal 1 inch diameter Pyrex pipe. Entrance and exit connections for gas flow are 1/4 inch pipe nipples welded to steel end flanges attached to the glass pipe.

Attempts to obtain absorption data from this apparatus were unsuccessful. Problems were encountered preparing the fused salt mixtures and maintaining a homogeneous melt. Little or no absorption was observed when a humidified flue gas containing 3,000 ppm SO_2 was passed over the melt.

The test results are shown graphically in Figure 4 as percent SO_2 absorbed (100 percent = 3,800 ppm) versus time. At 3 percent by weight CaO, the SO_2 removal decreased logarithmically with time. On increasing the CaO content to 5 percent, the SO_2 removal became nearly linear with time, indicating that something more than an increased surface concentration of reactant was involved.

A small, stirred reactor was assembled after attempts to correct the horizontal reactor were unsuccessful. This apparatus, shown in Figure 5, was essentially a one-liter, round-bottomed flask, having three ground joint connections. A flat, stainless steel paddle stirrer was held in the center of the flask and inlet and outlet tubes were attached to the other connections.

A thermocouple well was added to the outlet tube connection in a subsequent modification to check gas and melt temperatures. Simulated stack gases were introduced about 2 inches above the melt and 1 inch off center of the reactor. The gas volume was approximately 1 liter, when a 300 g charge was placed in the reactor.

Regeneration

Thermal and carbothermic regeneration processes were examined in a Cahn electrobalance. TGA experiments were done in an air furnace capable of operating to 2000°F. The balance is capable of measuring weight differences as small as 1 µg in the 100 mg range. The apparatus, as prepared for TGA experiments, is shown schematically in Figure 6. The general procedure for these tests was to obtain a fairly representative sample in the 100 mg weight range and follow the weight changes occurring as the sample was heated in a linear thermal gradient of approximately 5°C per minute.

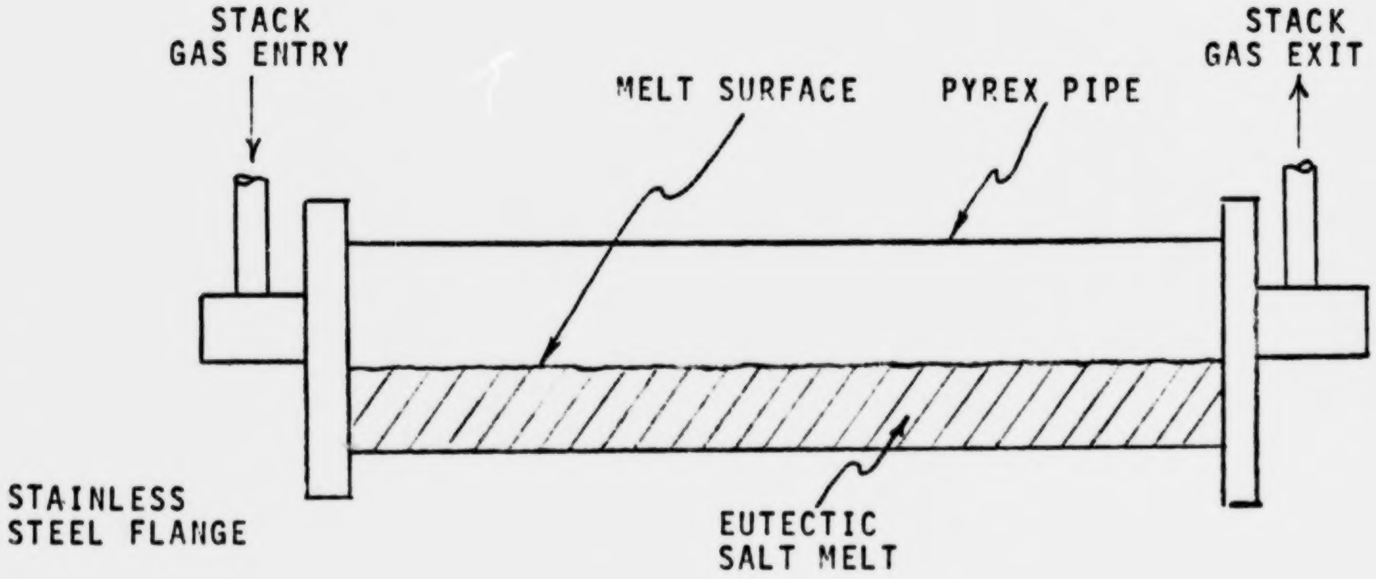
STACK
GAS ENTRY
MELT SURFACE
PYREX PIPE
STACK
GAS EXIT
STAINLESS
STEEL FLANGE
EUTECTIC
SALT MELT

FIGURE 3 - Horizontal Tube Reactor

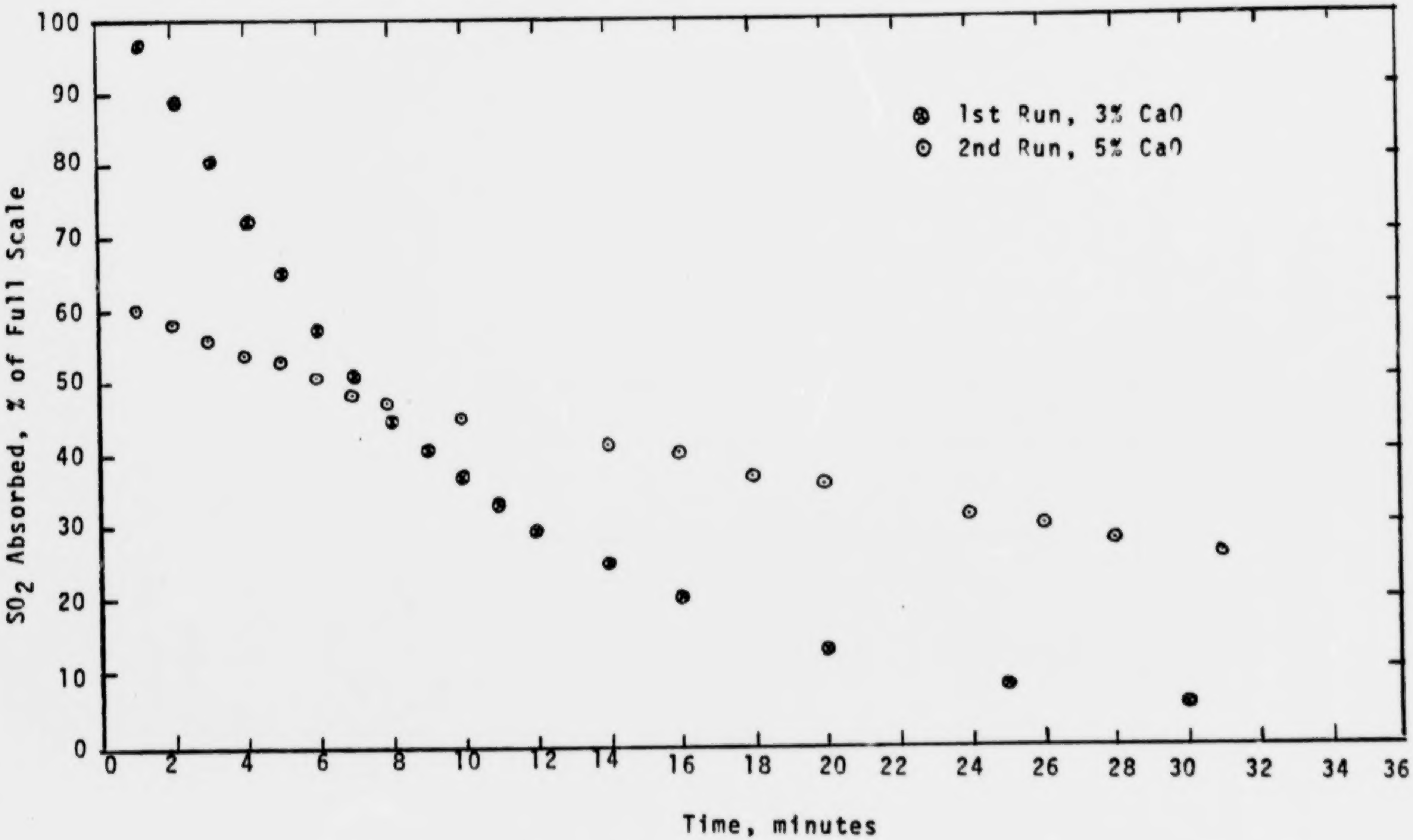

FIGURE 4 - SO_2 Absorbed vs Time for Horizontal Tube Reactor

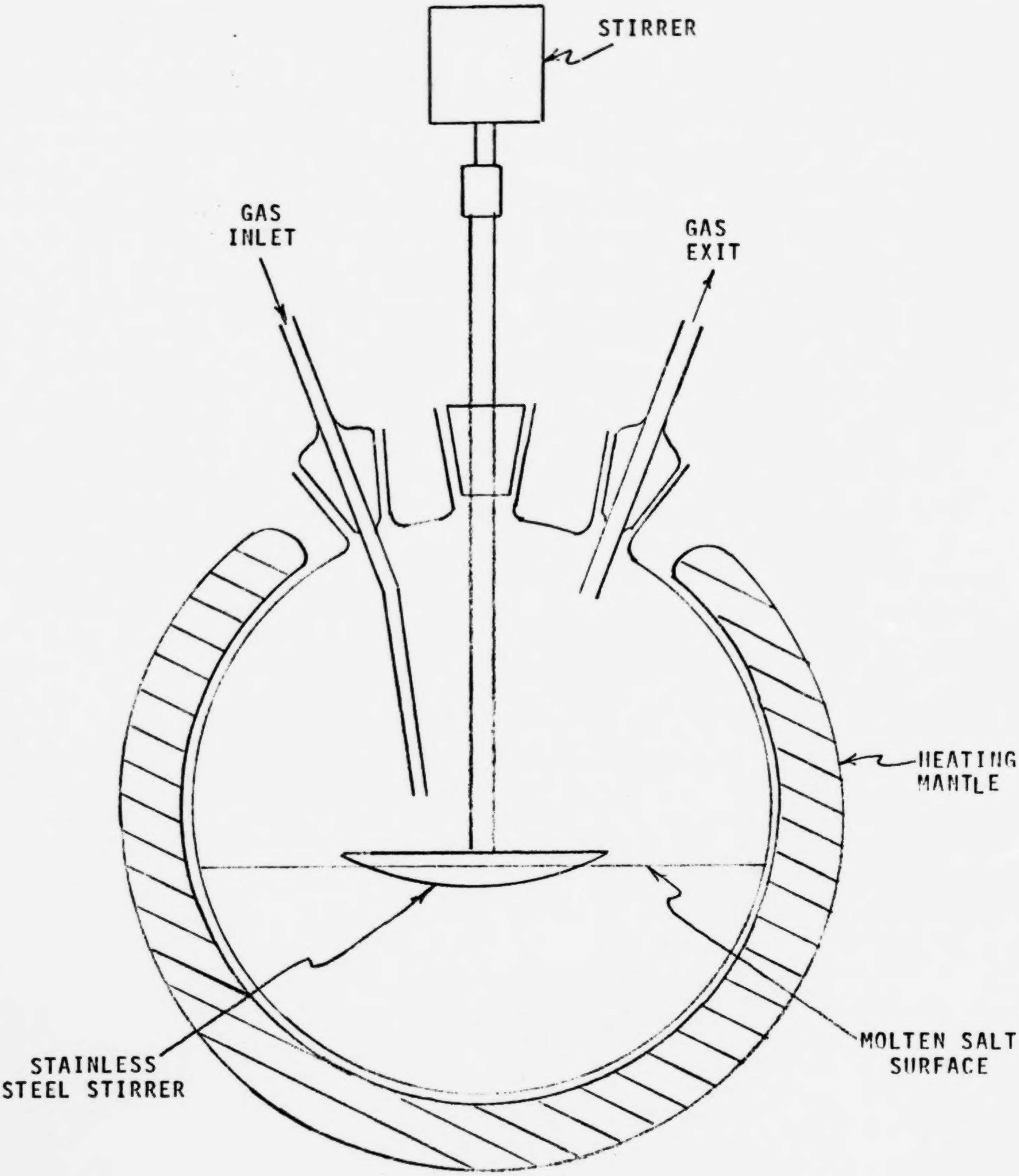
STIRRER
GAS INLET
GAS EXIT
HEATING MANTLE
STAINLESS STEEL STIRRER
MOLTEN SALT SURFACE

FIGURE 5 - Stirred Reaction Vessel

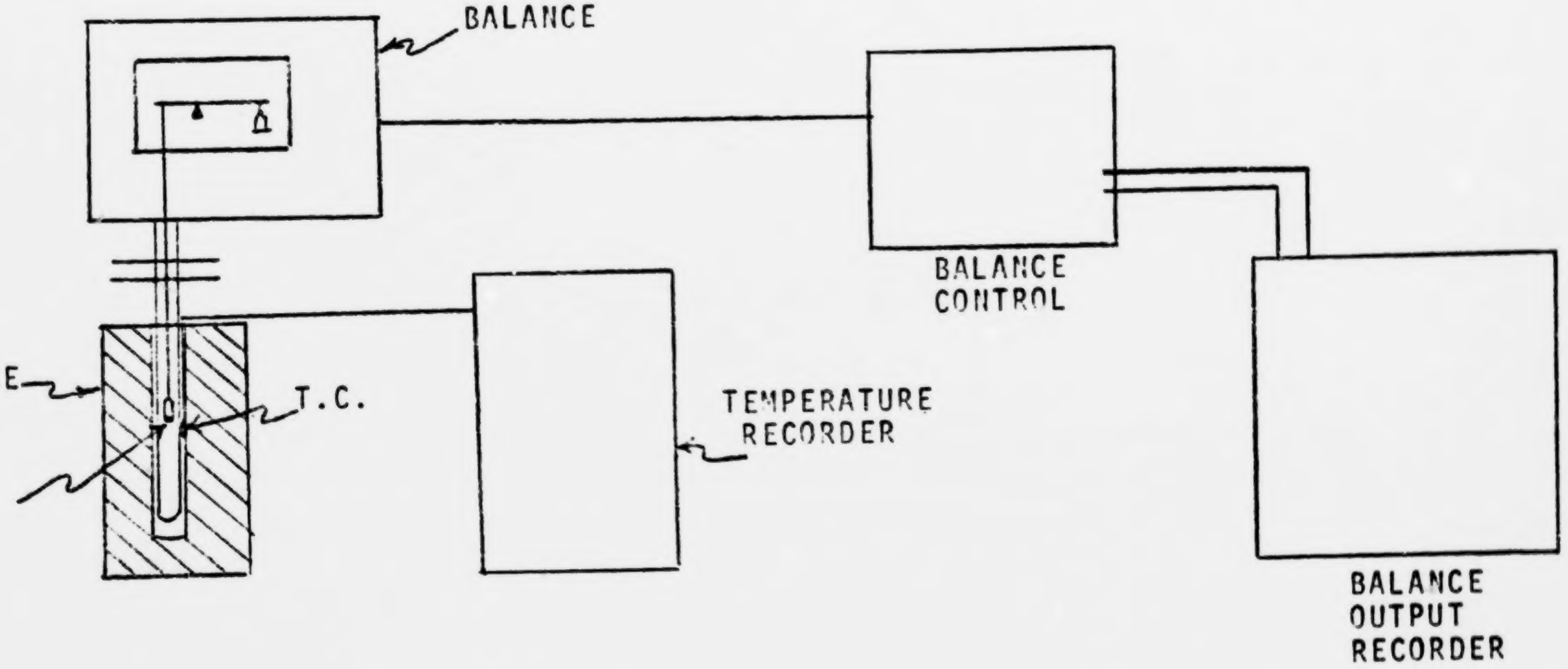
BALANCE
BALANCE CONTROL
BALANCE OUTPUT RECORDER
FURNACE
T.C.
TEMPERATURE RECORDER

FIGURE 6 - TGA Apparatus

Chemical regeneration studies were carried out in the apparatus shown in Figure 7. This was similar to the bubbler apparatus used for absorption studies with the exception that pure N_2 was used as a carrier gas and the system was thoroughly flushed with N_2 to obtain a blank SO_2 value prior to the addition of solid $NaPO_3$ granules. The "spent melt" was either that removed directly from the bubbler apparatus or the concentrated absorption products obtained by filtering through a 15 μ micrometallic filter.

Original solubility estimates were made on the basis of 15 g eutectic samples by visual observation of the salt additions and tare-weighting of the added material. Saturated solubilities were later obtained on 60 g samples of the eutectic salts after 30 minutes equilibration at the designated temperature. Standard wet-chemical analyses were performed on aliquot samples poured from these melts.

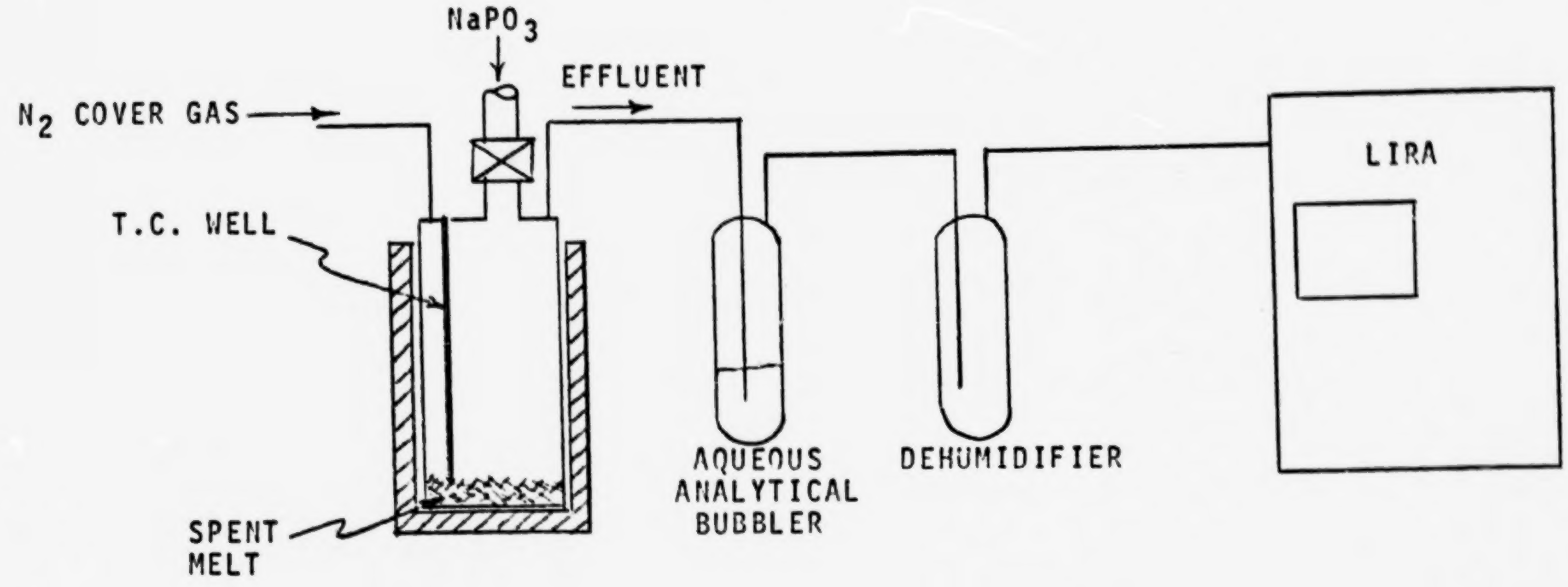
$NaPO_3$
N_2 COVER GAS
EFFLUENT
T.C. WELL
SPENT MELT
AQUEOUS ANALYTICAL BUBBLER
DEHUMIDIFIER
LIRA

FIGURE 7 - Chemical Regeneration Apparatus

INITIAL SCREENING AND COMPATIBILITY TESTS

The initial selection of low-melting fused salts for candidates in SO_2-scrubbing systems was made on the basis of gross compatibility tests. A few eutectic systems were selected on the basis of melting points and thermodynamic calculations for exposure to pure SO_2. These eutectics were exposed in the apparatus shown in Figure 8 where pressure measurements were made in the flue gas temperature range.

The glass apparatus permitted visual observation of any reaction occurring in the melt. A measured amount of SO_2 was admitted to the container and PVT calculations were made at the various temperatures to verify that the molten salt was chemically inert.

The data from the compatibility tests are summarized in Table II. None of the low-melting eutectics tested was completely inert towards pure SO_2. Solubility of SO_2 was assumed in those cases where there was no visible reaction and pressure measurements were lower than calculated. These "solubilities" were almost within the accuracy of experimental measurements and negligible at ambient pressure.

Since none of the fused eutectics was inert towards SO_2 at stack gas temperatures, various acid-base and redox reactions were investigated as means to stop the stack gas-solvent interactions. The combination of low SO_2 concentrations in stack gases and the dissolution of reactive "sorbents" in the fused eutectics has resulted in making fused inorganic liquid systems which would reduce most pollutant concentrations into the range of 0-300 ppm.

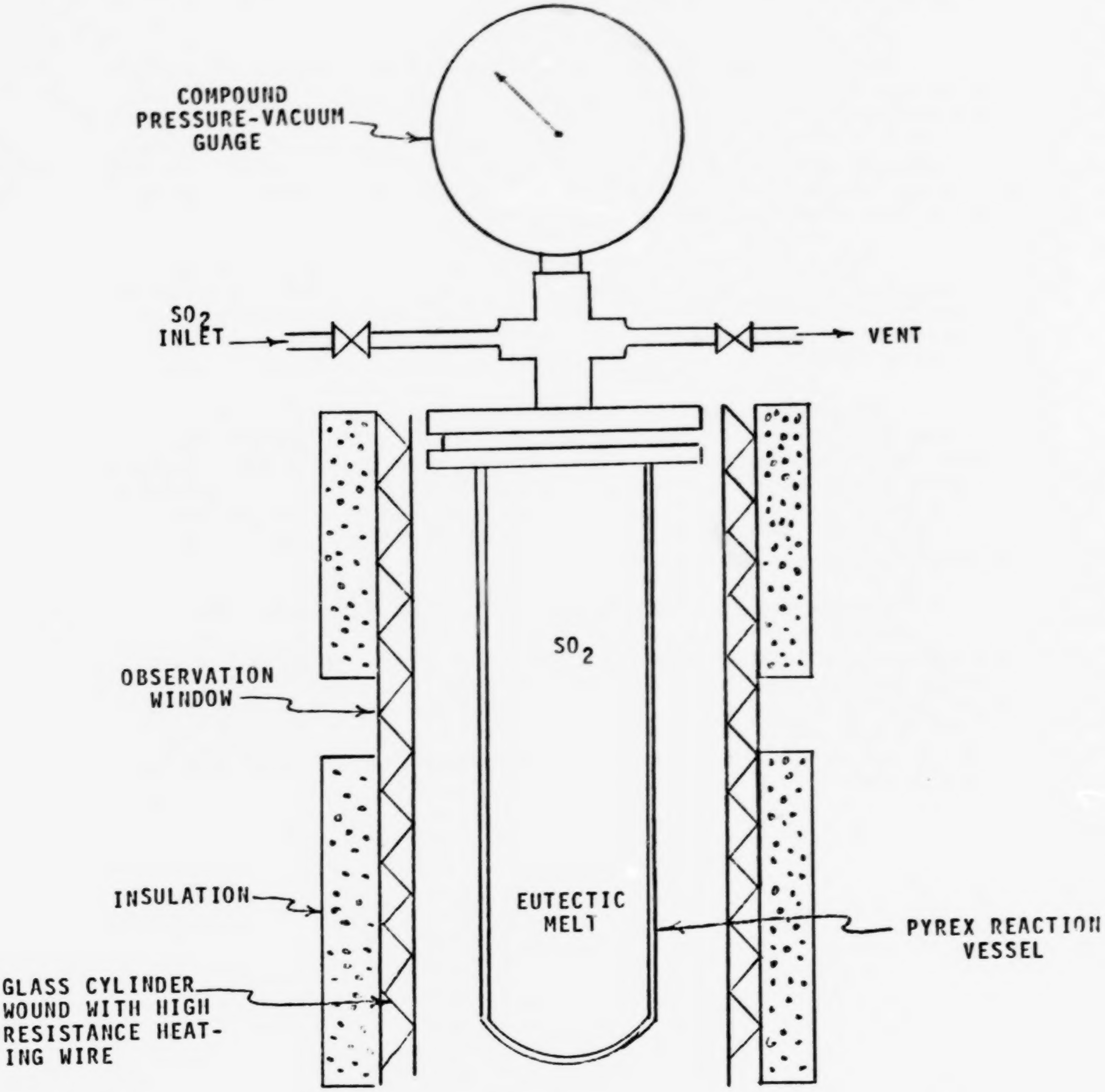
COMPOUND PRESSURE-VACUUM GUAGE
SO2 INLET
VENT
SO2
OBSERVATION WINDOW
INSULATION
EUTECTIC MELT
PYREX REACTION VESSEL
GLASS CYLINDER WOUND WITH HIGH RESISTANCE HEATING WIRE

FIGURE 8 - Apparatus Used in Rough SO_2 Compatibility Tests

TABLE II - BUBBLER SCREENING TESTS OF FUSED INORGANIC ABSORBERS EXPOSED TO SIMULATED STACK GAS

Melt	Reaction Temperature (°F)	Remarks
KNaZnAc	300-380	Decomposes at 410°F to yield a gas.
NaAc	160	Decomposes at 400°F
KAc	180	Decomposes at 650°F
KNO_3-$LiNO_3$	300	Some NO_2 evolved
KLiCl	720	Cl_2 evolved
$KNaLiNO_3$	280	NO_2 evolved
$NaKLiNO_3$ + $BaCrO_4$	260	Absorption good, but NO_2 also evolved
B_2O_3	600	Viscosity and Δ P too high
$CdNaLiNO_3$	270	Reacts, releasing NO_2
$KHSO_4$	500	Poor SO_2 absorption
KCNS	350	Effective SO_2 absorbent, but H_2S and other gases released
$LNaLiNO_3$ + $BaCrO_4$ + BaI_2	300	Good SO_2 absorption, releases NO_2
KCl-$ZrCl_4$	200	Decomposes
KCNS-NaCNS	260	Good SO_2 absorption but H_2S liberated.
KNO_3-$LiNO_3$ + ZnO	280	Easily slurried, but absorption rate poor.
KNO_3-$LiNO_3$+ BaO	200	Irregular absorption
KNO_3-$LiNO_3$ + MgO	280	Poor absorption rate
Urea-8KNO_3-20$NaNO_3$	160*	SO_2 effectively absorbed but NH_3 evolved.
KNO_3-$LiNO_3$ + CaO, $CaCO_3$ or $Ca(OH)_3$	270-280	Good absorption

*The operating temperature can be reduced significantly below that of the anhydrous ternary eutectic, when it is exposed to water vapor.

Intentionally Blank

MOLTEN SALT SYSTEMS

The basis for inorganic molten salt schemes developed during this program has been the reactive absorption of SO_2 in fused salt media by Lux-Flood acid-base reactions. A competition between acid-base and redox reactions has resulted in some deleterious side reactions evolving NO_x or halogens in most cases, but proper selection of solvent and reactive species can realize a selective absorption of SO_2.

Reaction Chemistry

In addition to the general absorption reactions [(a) and (b)] taking place in the candidate SO_2-absorption schemes, several other reactions are possible within any system. The reactions listed below represent the most probable reactions which may occur in a molten salt system. We have identified what we feel are the most important reactions and performed experimental tests to generate data which would elucidate the extent and rates of reaction.

a) $CaO + SO_2 + 1/2O_2 \longrightarrow CaSO_4$

b) $CaO + SO_2 \longrightarrow CaSO_3$

c) $CaO + NO_2 \longrightarrow CaNO_3$

d) $CaO + NO \longrightarrow CaNO_2$

e) $CaO + CO_2 \longrightarrow CaCO_3$

f) $CaCO_3 + SO_2 \longrightarrow CaSO_3 + CO_2$

g) $CaCO_3 + SO_2 + 1/2O_2 \rightarrow CaSO_4 + CO_2$

h) $CaCO_3 + NO_2 \longrightarrow CaNO_3 + CO_2$

Several tests were made to establish the relationship between the oxide-ion (CaO) concentration and the extent of reaction that occurs with the nitrate solvent, releasing NO_x. In all these tests it appeared that the solvent-SO_2 reaction is more dependent upon the water concentration than the oxide-ion concentration. The possibility exists that the first exposure of the melt may also include reactions of the oxide with other acid stack gas constituents such as CO_2. Additionally, there are many possible interactions of SO_x-NO_x-H_2O-CO_2 within this system under stack gas operating conditions. The initial release of NO_x from nitrate melts and halogen melts and halogens from halide melts may signify a competition between redox and acid-base reactions in these systems before the water-equilibrium is attained.

The absorption of water vapor is well known for alkali nitrates. Hull and Turnbull (1970) reported the solubility of water in nitrate-nitrite melts up to approximately 280°C.

All indications are that a short (5-10 minute minimum) equilibrium is required during which equilibrium NO_x-SO_x-H_2O concentrations are being established in these systems.

NO_x concentrations between 5 and 500 ppm have been observed during the first 5 minutes of operation. After 10 to 15 minutes the NO_x concentration has decreased to almost negligible (~1 ppm) quantities and remains relatively stable until the oxide-ion concentration is depleted. The time for delivering a measurable amount of NO_x and the coinciding SO_2 concentration are shown for various CaO concentrations in Table III. Even after the SO_2 concentration increases above 1,000 ppm the amount of NO_x evolved is quite small (~5 ppm). NO_x is always released at the 5-100 ppm level during the first few minutes of operation.

The results of these tests for NO_x evolution and previous tests for absorption efficiency are in good agreement. CaO-nitrate systems have been shown to release slightly less NO_x than $Ca(OH)_2$-nitrate systems. This order was also revealed in the tests measuring SO_2-absorption efficiencies. The results for both series of tests agree with the reaction model used in preliminary screening calculations where the absorption reaction was assumed to occur through the Lux-flood, acid-base reaction. Within this reacting medium the oxide-ion donors would be rated as $CaO > Ca(OH)_2 > CaCO_3$.

Some differences have been observed among the various nitrate eutectic solvents also. When exposed under similar conditions with CaO as the oxide-ion donor, the (Ca-K-Na) NO_3 eutectic released the least amount of NO_x and had a very short (~5 min) equilibration time. The maximum NO_x evolved during the equilibrating period was only slightly less stable towards SO_2 but the urea-KNO_3-$NaNO_3$ and (K-Na-Li)NO_3 eutectics released NO_x at concentrations in excess of 100 ppm for longer periods of time. Although only slight differences from these trends were observed when either $Ca(OH)_2$ or $CaCO_3$ were added as the oxide-ion donor, none of these systems displayed the stability towards the stack gas of an equivalent system containing CaO. In the case of the (Ca-K-Na) NO_3 eutectic, which holds an excessive amount of water, the differences between CaO and $Ca(OH)_2$ are minimal.

While attempting to extend the utilization of the CaO, it was noted that the absorption of SO_2 took place in two definite "stages". As shown schematically in Figure 9, the first "stage" is highly efficient in SO_2 absorption, with exit

TABLE III - NO_x AND SO_2 CONCENTRATIONS OVER MOLTEN SALT SCRUBBERS DURING INITIAL EXPOSURE

(Exposure to Stack Gas Containing 3.2% SO_2)

Molten salt composition	Time to release 5 ppm NO_x	Initial SO_2 concentration	Equilibrated SO_2 concentration
0.5 wt% CaO in (K-Na-Li)NO_3	1.1 (min)	>2000 (ppm)	<5 (ppm)
1 wt% CaO in (K-Na-Li)NO_3	2	150	60
2 wt% CaO in (K-Na-Li)NO_3	1.1	560	25
3 wt% CaO in (K-Na-Li)NO_3	1.3	180	25
4 wt% CaO in (K-Na-Li)NO_3	1.0	150	25
5 wt% CaO in (K-Na-Li)NO_3	1.0	150	25
6 wt% CaO in (K-Na-Li)NO_3	1.25	1050	30
5 wt% $Ca(OH)_2$ in (K-Na-Li)NO_3	2.1	140	25
5 wt% CaO in (Ca-K-Na)NO_3	2.5	140	25
5 wt% CaO in (K-Li)NO_3	3.0	100	25
5 wt% $CaCO_3$ in (K-Na-Li)NO_3	1.0	30,000	10,000

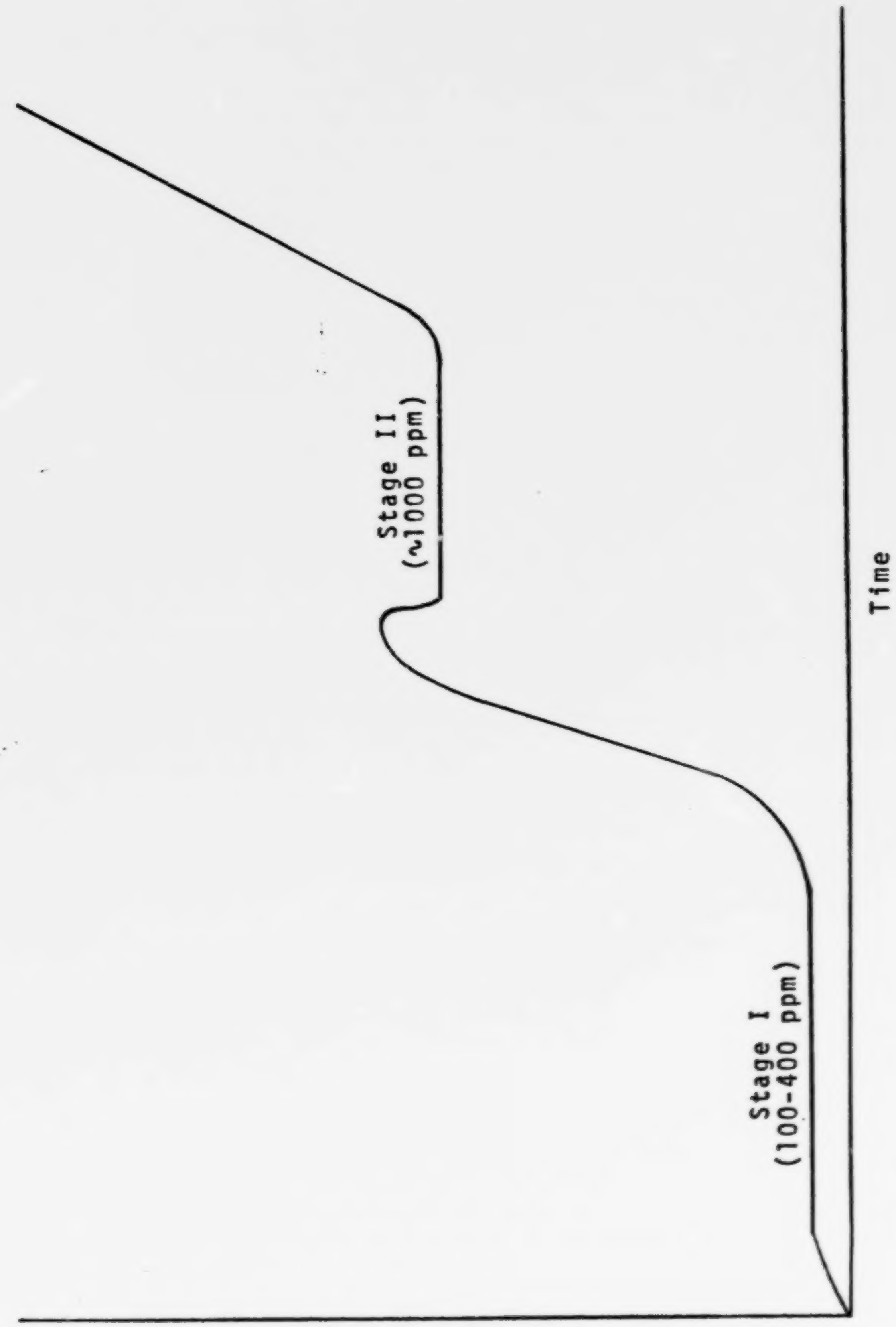

FIGURE 9 - Schematic Representation of SO_2 Absorption by Nitrate Melt Charged With Calcium Oxide

concentrations in the 150 to 400 ppm range. The second "stage" or plateau is much less efficient, giving exit concentrations in the order of 1,000 ppm SO_2.

To confirm the speculation that the second "stage" was due to conversion of the oxide to carbonate with the carbonate being less efficient at scrubbing SO_2, a reaction charge was made up with the same amount of $(K,Li)NO_3$, but containing 5 percent $CaCO_3$. By running a flue gas absorption under identical flow and contacting conditions, the second "stage" of the oxide absorption curve was nearly reproduced. Thus it appears reasonably certain that attempting to extend the utilization of CaO in a single stage reactor results in conversion of more oxide to carbonate with a loss of scrubbing efficiency.

To obtain further information, an experiment was made in which incremental additions of CaO were made to a (K,Li) nitrate melt with SO_2 absorption measured after each addition. The original charge to the spray agitator reactor was 300 g $(K,Li)NO_3$) with 9.3 g of CaO (3 percent). This was allowed to absorb SO_2 only through "Stage I". Incremental additions of CaO, using 3 g increments, were then made, absorbing SO_2 after each addition. A total of 12 such additions were made, giving an equivalent of 13 percent by weight CaO. No significant differences in SO_2 adsorption could be discerned for the individual increments and, more surprisingly, no severe increase in viscosity was observed.

Thus it appears that in a circulating system, continuous CaO additions could be made, with a bleed stream removing product-rich melt for regeneration. Such a system could work at a nominal loading of 10 percent CaO and a utilization of 30 percent to 35 percent in the first "stage" of absorption, thus being equivalent to the assumption of 60 percent utilization of 5 percent CaO loading.

For comparison, a 300 g $(K,Li)NO_3$ melt was loaded with 45 g CaO (added all at once) and tested in the same single stage spray contactor. The initial viscosity of the melt plus oxide was about the same as the final viscosity of the run made incrementally. However, after SO_2 absorption, the melt was extremely viscous, being quite difficult to stir or pour. This result shows that the rate of addition of CaO to the carrier melt in a circulating system will possibly be a critical factor in maintaining a workable fluid system.

In general, the nitrate systems containing stable hydrated salts combined with the strongest oxide-ion donor (CaO) showed the best stability towards the simulated stack gas and the best SO_2-scrubbing efficiencies.

Fly Ash Compatibility Studies

Fly ash samples were added to each of the molten salt candidate melts to determine their compatibility. In each case, the fly ash settled out quickly with only slight indications of slurry formation and no evidence of exothermic chemical reaction.

Stirring produced a suspension in the $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic, similar to the CaO absorbent. Stirring the ternary alkali metal nitrate or urea-KNO_3-$NaNO_3$ eutectics produced a suspension, but this settled more quickly than the $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic.

Samples taken from these melts contained 1-6 weight percent water-insoluble materials. The $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic contained the most water-insoluble material (6 weight percent), while the binary alkali metal nitrate contained $\sim$1.5 weight percent, the ternary alkali metal nitrate $\sim$2 weight percent and the urea -KNO_3-$NaNO_3$ contained $\sim$2 weight percent.

Addition of fly ash to the ternary alkali metal nitrate eutectic caused the most vigorous gas evolution. This was attributed to the water content of the fly ash. Although the KNO_3-$NaNO_3$-$LiNO_3$ eutectic is hygroscopic at ambient temperatures, the fused salt becomes nearly anhydrous. These characteristics have been noted previously with the alkali nitrate eutectic salt mixtures and differ from the more hydrophilic $Ca(NO_3)_2$-containing fused salt candidates.

A 10 weight percent addition of fly ash was placed in the molten lithium-sodium-potassium nitrate eutectic to measure interactions. Total sulfur analyses of the fly ash gave approximately 3 weight percent SO_3. During a fifteen minute exposure to the molten nitrate eutectic better than 90 percent of the sulfur content was transferred to the fused salt. This transfer was found to occur through the formation of alkali metal sulfates and sulfites, and the dissolution of some $CaSO_4$.

Similar tests were done to measure the transfer of carbon in fused salt-fly ash interactions. Carbon analyses of the fly ash were done with a Leco C-analyzer on samples of fly ash before and after exposure to fused salts.

The carbon content of fly ash "as received" from a power plant was 2.2 percent. After exposure to the potassium-lithium binary nitrate the carbon content was reduced more than 63 percent. When placed in the ternary eutectic (potassium-sodium-lithium nitrate), the fly ash was more than 70 percent decarburized.

When the mixture (K-Na-Li)NO_3 + 3 weight percent CaO + 10 weight percent fly ash was used in a bubbler to scrub a simulated stack gas containing 32,000 ppm SO_2, the water-insoluble fraction contained 4.3 percent carbon. A slight increase would be the result of SO_3 transfer and $CaSO_4$ dissolution, but this 95 percent increase must be the result of CO_2 absorption. A working hypothesis has been that those sites, previously occupied by SO_3, are now open to absorb CO_2.

Comparative Absorption Studies

Six separate absorption tests were done in the bubbler system, with CaO concentrations varying from 1 to 10 weight percent in the (Ca,K,Na)NO_3 eutectic. The results of five of these tests are presented in Figure 10, where the scale reading of the SO_2 analyzer is plotted against time. The dotted line at scalar 8 on the ordinate indicates the 400 ppm mark or 95 percent removal of SO_2.

The results of these tests reaffirmed the rough screening tests, in that eutectic salt mixtures containing between 2 and 5 weight percent CaO exhibit the best absorption properties. As shown in Figure 10, mixtures containing less than 2 weight percent CaO do not absorb SO_2 readily and are quickly exhausted. This may be attributed to the low concentration of CaO and the infrequent collisions of the reactants.

Salt mixtures containing more than 5 weight percent of CaO have shown poor capabilities as absorption media also. As shown in Figure 10, these mixtures have minimum retention and SO_2 is rapidly transferred through the melt and found in the effluent. This may result from the increased viscosity of the melt which inhibits bubble dispersion and mass transfer within the melt.

Comparison studies made in the stirred reactor have shown somewhat similar trends over a more narrow range of concentrations. Absorption runs were made under similar operating conditions (SO_2 flow rate and agitation) at CaO concentrations of 1 percent, 3 percent, and 5 percent in the (K-Li)NO_3 binary and of 5 percent in the (Ca,K,Li)NO_3 ternary system. In the binary K-Li system, the maximum absorption rate was observed with 3 percent CaO. At 5 percent CaO, the rate of absorption was similar for both solvent systems, however, the absorption lifetime was greater for the (Ca,K,Na)NO_3 ternary system.

Eutectic salt mixtures containing from 3 to 5 weight percent CaO gave the best results in bubbler tests. Several of these mixtures were tested in the bubbler apparatus to determine the affect of fly ash on chemistry of the absorption.

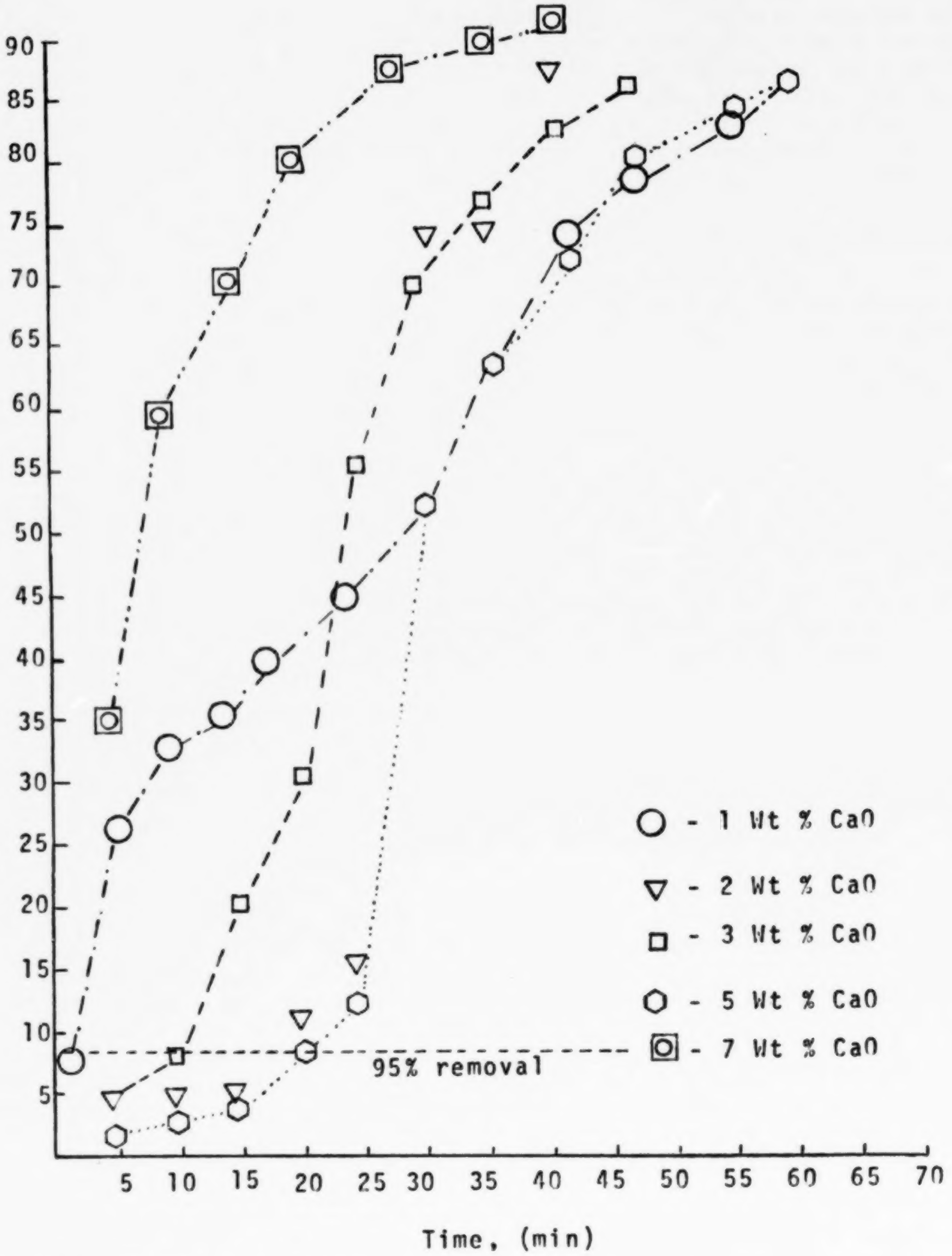

FIGURE 10 - Absorption Characteristics of the $Ca(NO_3)_2$ - KNO_3-$NaNO_3$ Eutectic Containing Different Concentrations of CaO Reactant

A comparison of the scrubbing efficiencies is presented graphically in Figure 11 as effluent SO_2 concentration in ppm versus time. Each of the tests was done using the KNO_3-$NaNO_3$-$LiNO_3$ eutectic which had been fused and the reactive species added before exposure to the stack gas. In each test, the melt was held at a nominal temperature of 300°F and stack gas containing 8,700 ppm SO_2 was bubbled at a rate of 1.6 l/min.

As shown in this figure, the ternary alkali nitrate eutectic containing 5 weight percent CaO removed 95 percent of the SO_2 concentration from the stack gas mixture for more than 60 minutes. The effluent SO_2 concentration slowly increased then, as the basicity of the melt decreases. Total exhaustion of the melt, to the point of negligible absorption, required 200 minutes.

No precipitate was observed in this salt mixture, but the sulfur-containing species was found to be $CaSO_4$. Approximately 1 weight percent of the sample taken from the melt was $CaSO_4$. The solubility of $CaSO_4$ in the ternary alkali metal nitrate was determined to be 1.2 weight percent which agreed well with data obtained in a separated solubility experiment. The total reaction required approximately 30 percent of the CaO available. Overall efficiency of the absorption process was approximately 40 percent.

The same unit containing 10 weight percent fly ash did not perform as well in the bubbler system. The 95 percent SO_2-scrubbing efficiency lasted for only 25 minutes. In addition to this decreased efficiency, exhaustion of the melt occurred more rapidly, allowing 100% of the SO_2 to pass through the bubbler after only 175 minutes exposure.

A slow rate of solution of either reactant or products could limit the useful lifetime of the CaO absorbent systems. This speculation was not confirmed, however, by a test in which a 5 percent CaO melt was run to completion and then allowed to equilibrate at operating temperature for 20 hours and retested for SO_2 absorption. A negligibly small additional absorption of SO_2 was observed, showing that solution equilibria have no apparent effect on absorbent life.

In the Phase I evaluation, it was assumed that an overall utilization of 60 percent of the CaO could be obtained at a nominal loading of 5 percent by weight in the molten nitrates. If the oxide utilization is limited to about 35 percent, for the most efficient scrubbing, then a higher recirculation rate or a higher oxide loading is required. Two tests were done to determine the influence of small oxide additions on the SO_2 absorption and the possibility of building up the CaO concentration as it was expended during exposure to a stimulated stack gas. Comparisons were made between bubbler and stirred reactor tests in which the concentration of CaO in the melt was periodically adjusted.

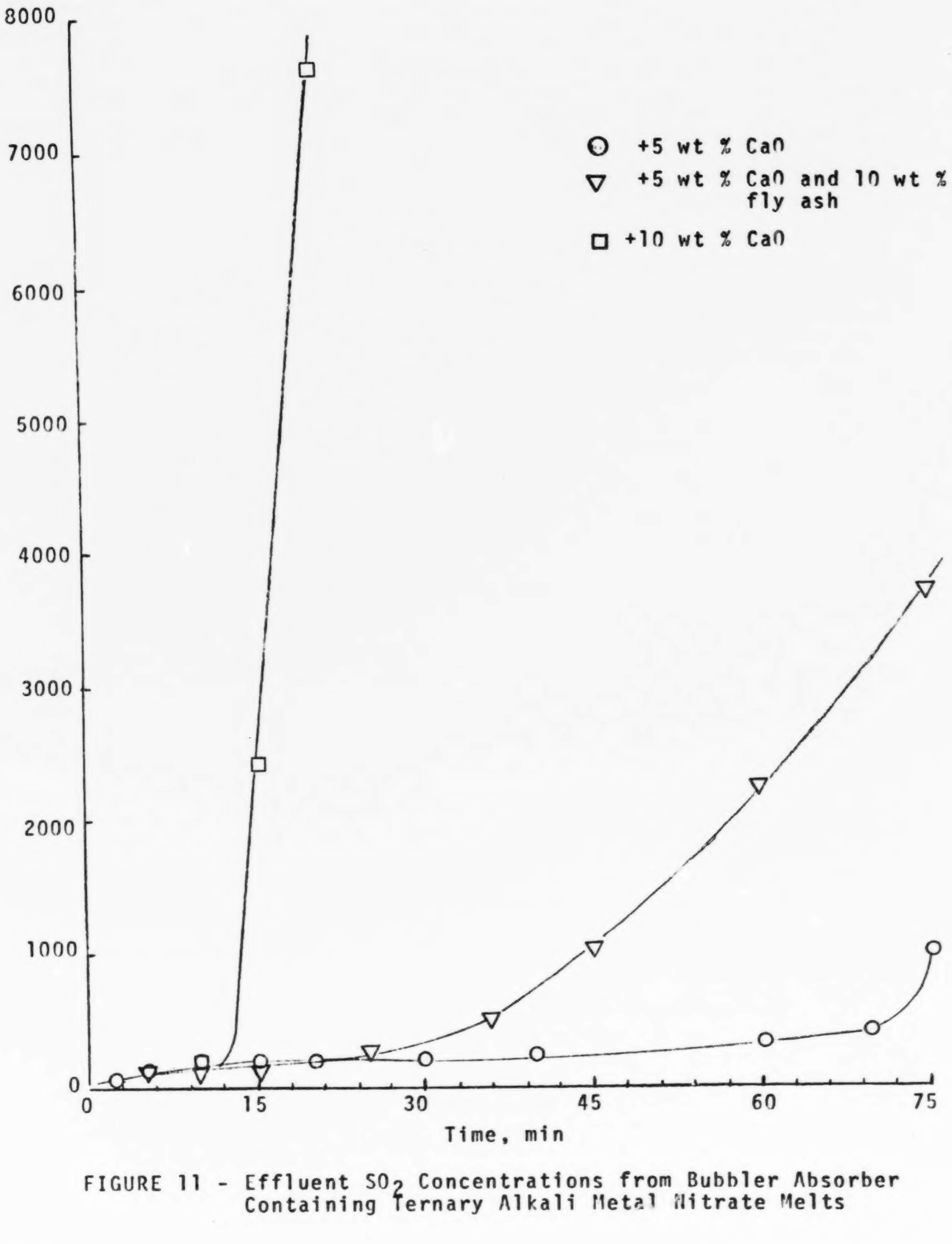

FIGURE 11 - Effluent SO_2 Concentrations from Bubbler Absorber Containing Ternary Alkali Metal Nitrate Melts

A (K-Na-Li)NO_3 eutectic mixture containing 5 weight percent CaO was prepared in the stainless steel bubbler for exposure to a stack gas containing 2.8 percent SO_2. A flow of 1.5 l/min was passed through the melt until the SO_2 content of the effluent wxceeded 2,000 ppm. The melt was filtered through a 15 µ pore size, micrometallic filter under nitrogen pressure into the concentric vessel.

After measuring the melt volume and calcium concentration, appropriate additions of eutectic salt and CaO were made to the filtrate to maintain the original concentrations. These additions were made to the melt, accumulating approximately 6.5 weight percent calcium (measured as CaO). After each addition of the molten salt solvent, the precipitate was stirred into the salt and allowed to equilibrate for thirty minuts before resuming the gas flow. The final filtration was carried out under nitrogen pressure, allowing the gas to remove as much of the solvent as possible.

The precipitate was removed from the filter and placed into sample bottles under dry nitrogen until ready for analysis. Sulfate, sulfite and sulfide were identified as the sulfur-containing products in the precipitate. Sulfite was the predominant S-containing product, being present at nearly ten times the amount of sulfate.

Carbonate was the main absorption product resulting from exposure to the simulated stack gas. It was found to be present at nearly twice the concentration of sulfite, the major sulfur-containing species. Neither hydroxide nor oxide remained in appreciable quantities in the precipitate collected from this test.

The earlier studies of the absorption reaction in the molten nitrates had shown only sulfate as the sulfur-containing reaction product, except in those reactions involving fly ash. The sulfite reaction product is more predominant in those runs in which the rate of absorption is maximized. It may be speculated that the initial reactionproduct is sulfite, according to the reaction

$$SO_2 + CaO \longrightarrow CaSO_3.$$

Subsequently, the sulfite may be oxidized, either by oxygen or by reaction with the nitrate melt, such as

$$CaSO_3 + 1/2O_2 \longrightarrow CaSO_4$$

or

$$CaSO_3 + NO_3^- \longrightarrow CaSO_4 + NO_2^-.$$

If the rate of oxidation of sulfite is somewhat slow relative to sulfite formation, attempts to maximize the SO_2 absorption would also result in higher $SO_3^=/SO_4^=$ ratios in the reaction products.

Samples of the precipitate formed during a 5 hour absorption test were analyzed for sulfate-sulfite ratios and the possible precipitation of S-containing products. As mentioned previously, the production of sulfite depends on the rate of absorption and the extent of loading. The precipitate from this test had a sulfite-sulfate ratio of 1.4.

The aliquot samples taken from the precipitate gave a range of sulfur values varying with location. Higher values were obtained on those samples taken from the bottom of the precipitate cake, indicating that settling is a possible means of concentrating the products.

Similar data were obtained on aliquot samples for the concentrations of $SO_x^=$ and carbonate. Mass spectrometer analysis on the gas mixtures evolved upon acidification gave CO_2/SO_2 ratios between 1.7 and 3.9. The majority of the results were in the range 2.0 ± 0.1.

Comparative Absorption Kinetics

Absorption into the fused salt systems has been measured under many conditions using several different methods. Initial tests were done with an unstirred, horizontal, tube contactor. Reproducibility of the measurements taken with this apparatus was unsatisfactory and a small, stirred reactor was assembled.

An apparent absorption rate was obtained for the CaO in ternary alkali metal nitrate eutectics by passing flue and smelter gases over the melt. The gas flow rate was adjusted to obtain a steady outlet SO_2 concentration without moving the surface of the liquid. These "steady-state" observations of apparent absorption rate have been used to calculate order-of-magnitude rates.

The apparent absorption rate is approximately 10^{-5} mmol SO_2/cm^2sec from these stagnant pool experiments. It must be emphasized that this rate is not a measure of the rate of the reaction between SO_2 and CaO, but rather a local absorption rate, measured under simulated operating conditions.

The data from these stagnant pool experiments can be used to calculate a mass transfer coefficient from the equation

$$N = Kg\ A\ \Delta P.$$

Including the partial pressure as a driving force term, the static mass transfer coefficient has been calculated at 4.0×10^{-6} mol/cm^2 sec atm for a 5 cm^2 surface area and 3.3×10^{-6} mol/cm^2 sec atm for a 45 cm^2 surface area.

More refined absorption tests were done using a stirred reactor, similar to that used by Shrier and Danckwerts (1969) in their studies of CO_2 absorption. The data obtained from tests using this apparatus are translated into absorption rates, using the formulas developed by Danckwerts (1965). The apparent absorption rates obtained may be compared with data reported by Hitchcock (1934) and Danckwerts and McNeil (1967).

Data obtained with the stirred reactor apparatus are in better agreement with Hitchcock's (1934) data for the absorption of CO_2 into caustic solutions. When the partial pressure of SO_2 in the flue gas is used as a driving force for the reaction, the mass transfer coefficient calculated for our system is 2.6×10^{-6} g mol/cm^2 sec atm. Hitchcock (1934) measured CO_2 absorption to occur in the range of 1×10^{-6} to 3×10^{-6} g mol/cm^2 sec atm.

An additional similarity between aqueous CO_2 absorption and fused salt absorption of SO_2 is the effect of viscosity. As the viscosity of the system increases (adding the reactive compound), the absorption rate goes through a maximum and decreases. This would indicate that the rate of reaction is quite rapid compared with the rate of diffusion into the liquid phase.

A series of tests were done to obtain the overall mass transfer coefficient for the simulated spray reactor. Operating at a fixed CaO concentration of 2 percent and, as nearly as possible, under identical spray contact conditions, SO_2 absorption runs were made under varying gas flow conditions. By correlating the time at which the exit concentration exceeded 500 ppm with the flow rate, a function was obtained which may be extrapolated to very high flow rates. A preliminary minimum value of the volumetric mass transfer coefficient, K_ga, of 0.17 lb moles/(hr)(ft^3)(atm) was obtained at a flow rate of 1 l/min.

Further experiments at several different gas flow rates, holding other experimental parameters constant, allowed a correlation of the log of the breakthrough time (T) with the volumetric flow rate (F). As shown in Figure 12, this resulted in a linear relationship. Extrapolation yielded a maximum value of F for this reactor configuration of 3.1 l/min. Using this F value and the nominal reactor volume of 1 liter, the calculated value for K_ga, the volumetric mass transfer coefficient based on the gas phase driving force, is 0.52 lb mole/(hr)(ft^3)(atm).

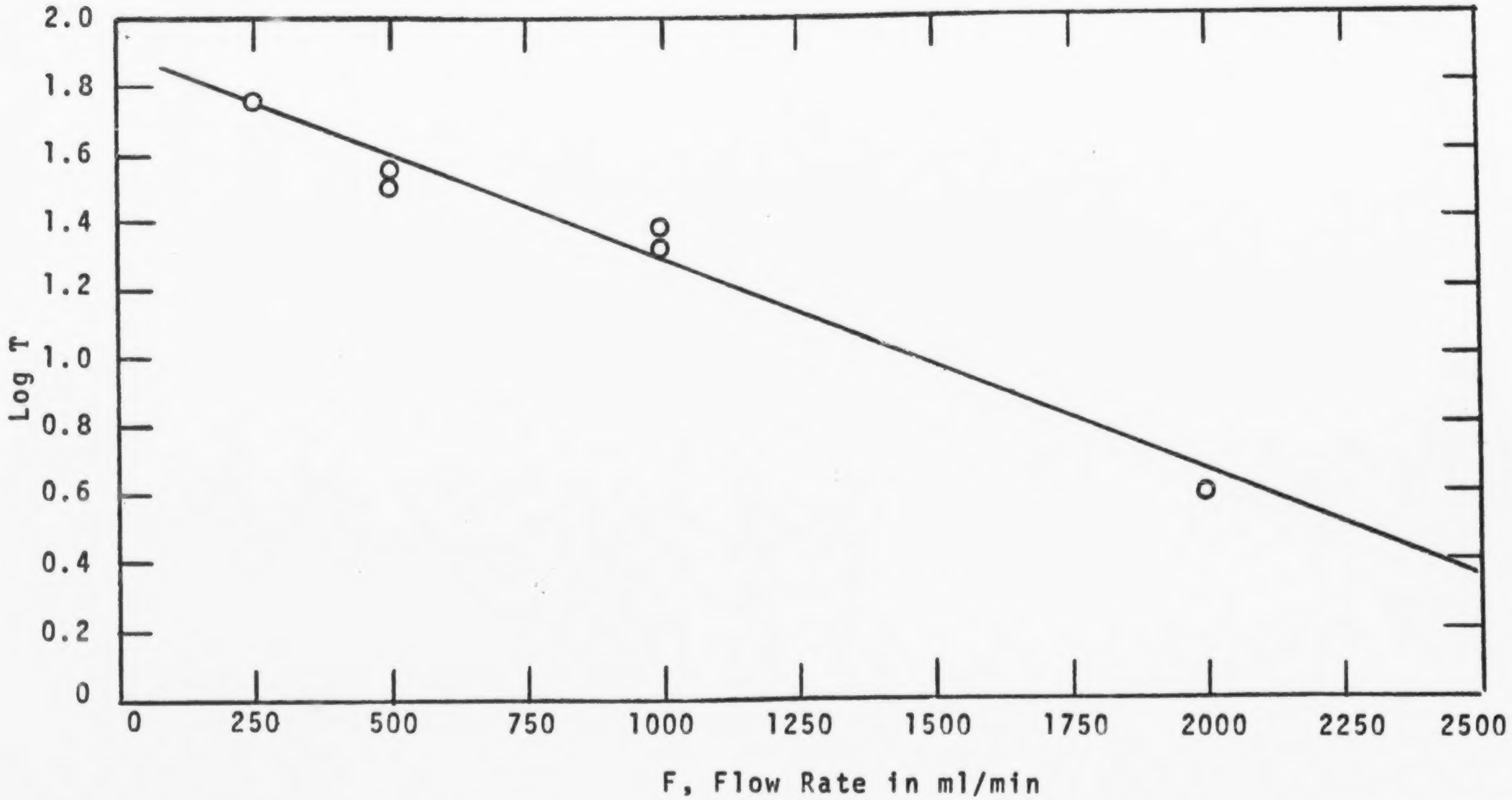

FIGURE 12 - Log of Breakthrough Time (T) Versus Flow Rate (F) for Simulated Spray Reactor

For comparison, K_ga values estimated from the data of Johnstone and Silcox (1947), on the absorption of SO_2 by alkaline solutions in a cyclone spray tower range from about 3 to 6 lb mole/(hr)(ft^3)(atm). The order of magnitude difference in K_ga is quite probably due to the larger effective absorption area per unit volume in Johnstone's apparatus. A controlled spray nozzle would be expected to give a much smaller and more uniform droplet than that obtained from our spray-type agitation.

In order to better compare the behavior of the Ca-molten nitrate system with known systems under more nearly similar hydrodynamic conditions, a series of experiments was made in which the absorption rate into still or slowly stirred solutions was measured. For these experiments, the comparison solutions were pure water and aqueous solutions of NaOH. Absorption rate comparisons were made under similar conditions of surface area, gas flow and agitation. The observed rates were compared with data from the literature.

The one liter reactor used for the spray contactor study was modified to allow absorption into a known surface area of liquid, either stagnant or slowly stirred so as to maintain an undisturbed liquid surface. With 150 ml of liquid in the reactor, the surface area was 85 cm^2. The gas used for this study was a mixture of SO_2 in nitrogen with a nominal SO_2 concentration of 800 ppm. This was used instead of the simulated stack or smelter gas in order to avoid the possible complication of CO_2 absorption.

The absorption of SO_2 in pure water was measured and compared with that calculated from the data of Whitman and Davis (1924), after correction for the difference in SO_2 concentration. As shown in Figure 13, the comparision is fairly good. Under the experimental conditions, the absorption by water showed a slight dependence on agitation and also showed a dependence on gas flow, increasing with increasing flow rate.

Under similar conditions, the absorption rates of SO_2 into 0.5 molal NaOH and into 0.25 and 0.5 molal CaO in $(L,Li)NO_3$ were measured. The aqueous runs were made at 68°F and the molten salt runs at 340-350°F. The results of these measurements are shown in Figures 14 and 15. With these systems, the initial absorption rates were practically independent of agitation (20 and 30 rpm) but did show a dependence on gas flow rate.

At gas flow rates of one l/min, the absorption rates of aqueous NaOH and both 0.25 and 0.5 molal $CaO-(K,Li)NO_3$ are quite similar. The 0.25 molal CaO system exhibits somewhat better absorption than does 0.5 molal CaO, possibly due to the higher viscosity of the 0.5 molal case. At higher flow rates, the

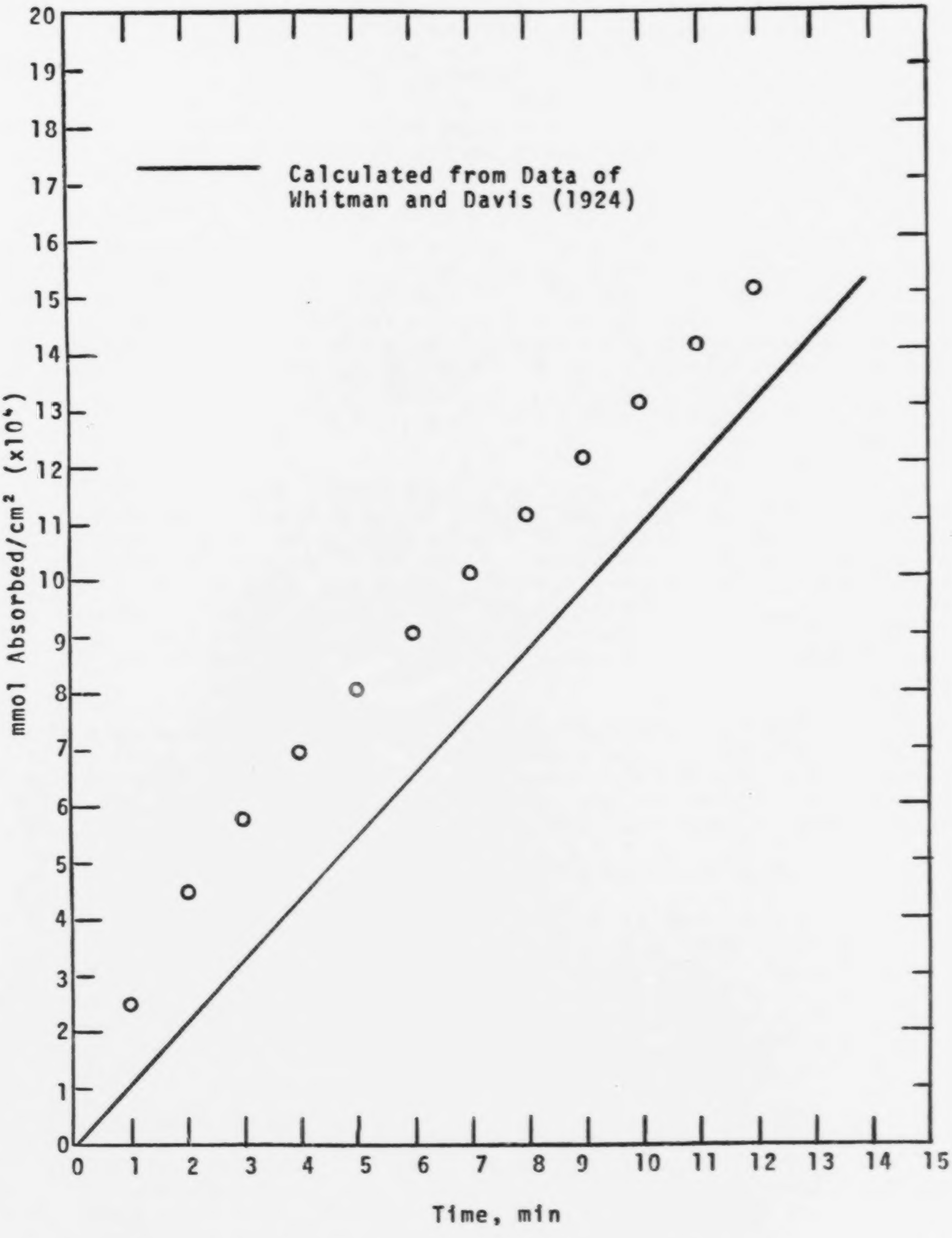

FIGURE 13 - Initial Absorption of SO_2 in H_2O

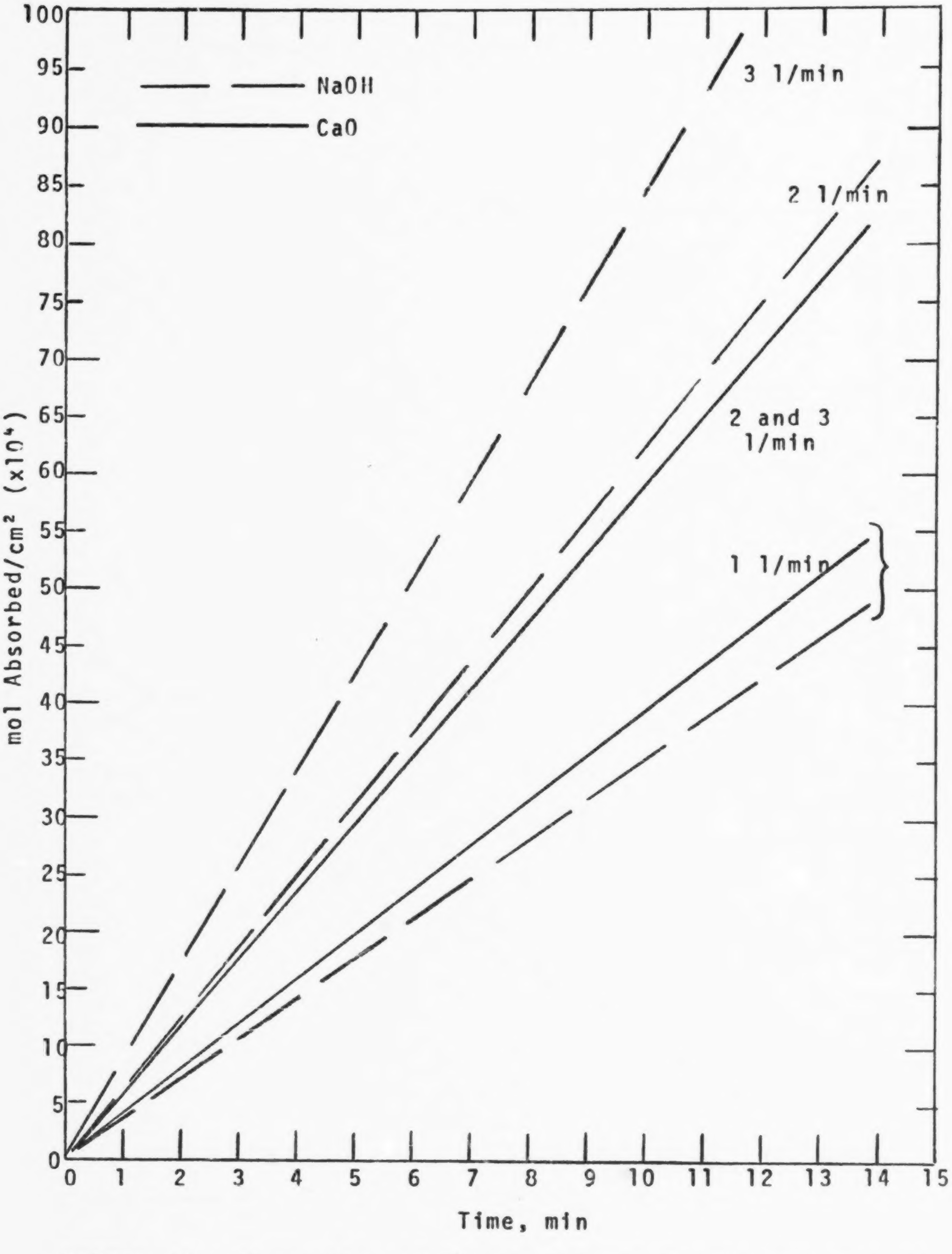

FIGURE 14 - Absorption of SO_2 by 0.5 Molal NaOH and by 0.25 Molal CaO-(K,Li)NO_3

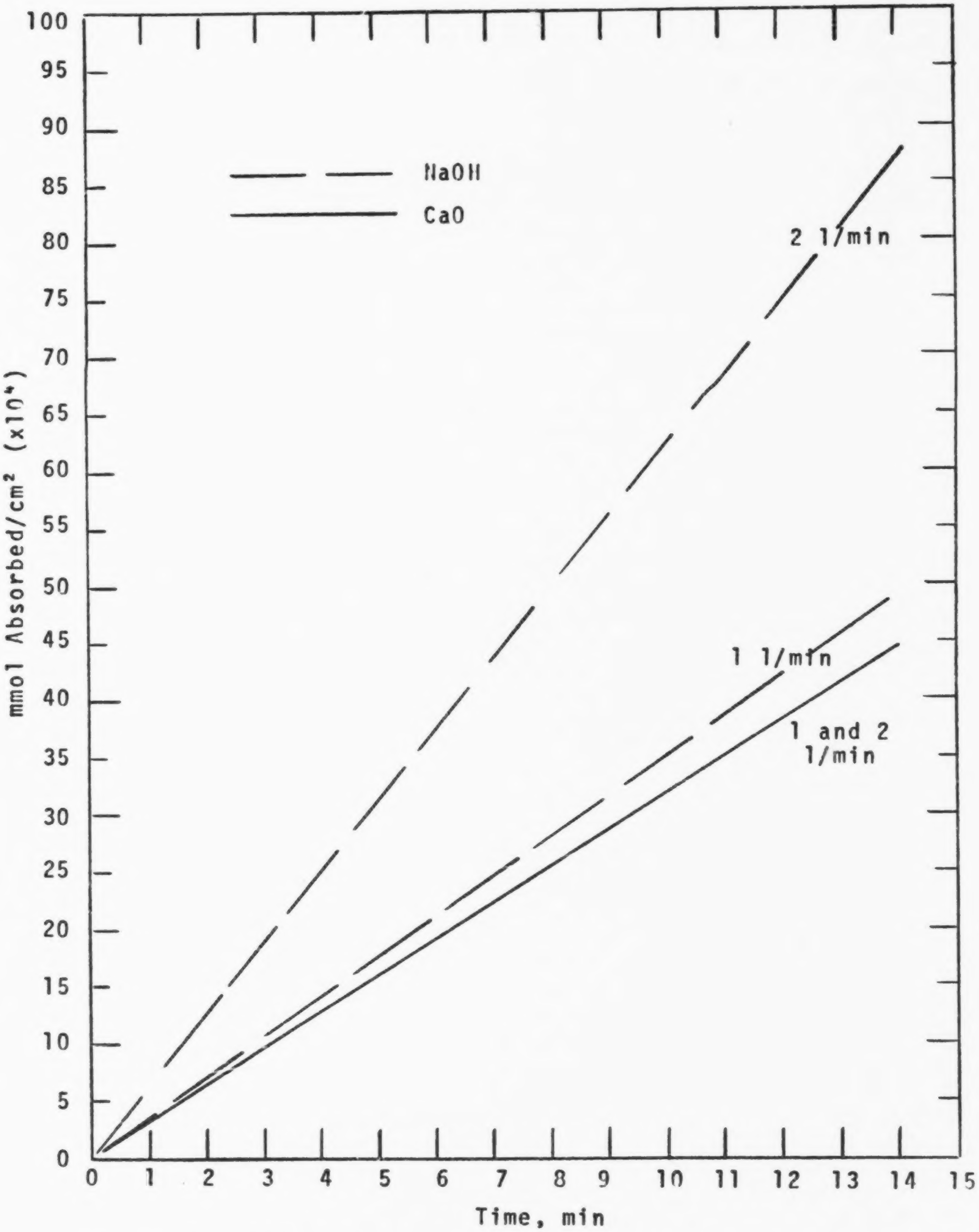

FIGURE 15 - Absorption of SO_2 by 0.5 Molal NaOH and by 0.5 Molal $CaO-(K,Li)NO_3$

aqueous system gives better absorption rates than does the non-aqueous system. This is not completely explained, although it was observed that in the non-aqueous system, a solid skin formed on the surface of the melt after the absorption had proceeded for a few minutes, creating an additional resistance to absorption. This surface skin, not identified, is possibly solid $CaSO_3$ and, if so, would form faster and interfere more markedly at the higher flow rates.

Under similar hydrodynamic conditions, the rate of absorption of SO_2 by the CaO-nitrate system is significantly better than that of pure water and approaches that of aqueous NaOH. Thus, it may be possible to use the available data on aqueous systems, such as that of Johnstone, in scaling the molten salt systems for engineering evaluation.

The general absorption characteristics of the molten nitrate-CaO systems are those of systems that are diffusion limited. The dependence of SO_2 absorption on CaO concentration and the observation of viscosity limitations at high CaO are consistent with the "liquid film" models in which there is a rapid second-order reaction with the absorption rate being limited by diffusion to and from a thin reaction layer within the liquid phase.

Cycle Tests of CaO-Nitrate System

In order to define more closely the operation of the molten nitrate-CaO system, a series of tests was made involving product recovery and melt recycle. In order to simplify the recovery procedure for this first test, no attempt was made to separate or enrich the absorption product before water washing. The total melt plus reaction products from the absorption step was digested with water and filtered to obtain the water insoluble products.

In the first test, 300 g (K,Li) NO_3 plus 6.2 g CaO (2 percent by weight) was exposed for one hour to the simulated smelter gas (nominal 3.2 percent SO_2) at a flow rate of one liter per minute, using the spray contact reactor. After completion of the absorption step, the total melt was digested with a preselected volume of hot water and filtered under slight vacuum. The insoluble products were dried to constant weight at 100°C and analyzed for Ca^{++}, $SO_4^{=}$ and total sulfur. The filtrate was evaporated to dryness to recover the nitrate salts for recycle. Fresh CaO was added to the recovered nitrates and the cycle was repeated. A total of four such cycles was made in this test.

In the first two cycles, the weight ratio of water to total melt was set at approximately 2.5 to 1. For the last two cycles, the amount of water was reduced to give a water to melt weight ratio of 2 to 1. The results of cycle test are summarized in Table IV.

TABLE IV - SUMMARY OF CaO-NITRATE CYCLE TEST

(K, Li) NO_3 added (g)	CaO added (g)	Water/melt wt. ratio	Recovered Product (g)	Product analysis, mmol/g		
				Ca^{++}	$SO_4^=$	Total S
1) 300.0	6.2	2.5	7.88	7.21	2.64	3.42
2) 0 (306 g recycle)	6.2	2.5	7.90	7.40	5.13	5.46
3) 0 (306 g recycle)	6.2	2.0	12.21	7.35	5.01	5.89
4) 3.0 (298 g recycle)	6.2	2.0	13.31	7.52	2.37	5.94

Total SO_2 through reactor 344 mmol

Total SO_2 recovered 221 mmol

The total weight of recovered insoluble product was a function of the amount of water used in the digestion and washing. Decreasing the water to melt ratio from 2.5:1 to 2:1 resulted in an approximate 50 percent in the weight of recovered product. The calcium concentration in the recovered product remained fairly constant from cycle to cycle, and after the first cycle, the total sulfur concentration also stabilized to a fairly constant value. The fourth cycle showed an unexplained greater proportion of sulfur as $SO_3^=$, but after the first cycle, the total amount of sulfur containing product, expressed as $CaSO_3$ and $CaSO_4$, ranged from 73 to 79 weight percent of the total recovered material.

Differentiation between $SO_4^=$ and $SO_3^=$ was made by wet analysis of two different samples of recovered product. One sample was directly acidified with a non-oxidizing acid to dissolve the sulfate and decompose the sulfite to SO_2. Sulfate was then determined by precipitation as $BaSO_4$. The other sample was oxidized with hydrogen peroxide in the presence of sodium carbonate to convert all of the sulfur-containing product to sulfate. The sample was then acidified and total sulfur determined as $BaSO_4$.

Because of the inoperability of the LIRA SO_2 analyzer during this test, no monitoring of the effluent SO_2 was made during the absorption cycles. However, the total amount of SO_2 passed through the reactor was well in excess of that for which efficient absorption have been determined to take place. The combined product analysis indicates that 64 percent of the calculated SO_2 passed through the adsorber was recovered as product.

A second series of cycle testing was run with a lower total exposure to SO_2 in each cycle, 30 minutes instead of 60 minutes, calculated to stay within the efficient absorption. Each cycle consists of a 30 minute exposure to smelter gas (nominal 3.2 percent SO_2) at a flow rate of one liter per minute, followed by water digestion, filtration and evaporative recovery of nitrate melt for recycle. The weight ratio of water to melt used for each cycle was held at 2 to 1.

The results of the first five cycles of the second series are summarized in Table V. There are several significant points of difference between these results and those reported for the first series. With the lower exposure time to SO_2, the absorption efficiency is much greater; 95 percent versus 64 percent for series I. The utilization of CaO, however, is much lower, and, as a result, the product is much lower in sulfur. The combined sulfite plus sulfate in the second series averages about 54 percent by weight as compared with about 75 percent in the first series.

Another significant difference in the product obtained is in the relative amounts of sulfite and sulfate in the two series. In the first series, the sulfate predominated; but in the

TABLE V - SUMMARY OF CaO-NITRATE CYCLE TEST, SERIES II

	$(K,Li)NO_3$ added (g)	CaO added (g)	Water/melt wt. ratio	Recovered Product (g)	Product analysis, mmol/g		
					Ca^{++}	$SO_4^=$	Total S
1)	300.00	6.2	2	9.14	10.29	0.28	4.28
2)	0	6.2	2	9.17	9.14	0.18	4.63
3)	0	6.2	2	9.58	8.69	0.18	4.52
4)	0	6.2	2	9.87	8.32	0.16	4.28
5)	0	6.2	2	8.26	8.90	0.18	4.54

Total SO_2 through reactor 214.5 mmol

Total SO_2 recovered 204.2 mmol

seocnd, the product is almost entirely sulfite. The long exposure time in the first series apparently resulted in considerable oxidation of the sulfite formed in the initial reaction.

The second series of cycle tests was terminated after 8 complete cycles of absorption and product recovery. No significant variations between cycles was observed nor was there any observable deterioration of the molten nitrate salt. Any changes of the nitrate salt due to interaction with the SO_2 were so slight as to be unnoticed. Thus, the conclusion is that as long as there is a small residual CaO concentration in the melt while exposed to the flue or smelter gas, the melt is not attacked. This qualitatively confirms the tests made of NO_x evolution from nitrate melts containing varying amounts of CaO.

Using wire mesh screens of several sizes between 100 mesh (150 micron opening) and 200 mesh (75 micron opening), tests have been made to determine the feasibility of filtration of product from the reacted CaO-nitrate melt. With both fresh and recycled melts, the products, and also the unreacted CaO, passed readily through all of the screen sizes tested. Thus, the product particle size is less than 75 microns and there is no significant particle growth due to recycle.

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EVALUATION OF NO_x-ABSORPTION POSSIBILITIES

In addition to the more prominent reactions with SO_2 occurring in these systems, reactions involving all of the acidic gases may be postulated. Absorption of SO_2 accrues through the use of Lux-flood acid-base reactions in the fused salt media. All of the reactions listed below may occur within these systems and have, under various conditions, been found.

REACTIONS IN FUSED SALT SYSTEMS

$$CaO + NO_2 \longrightarrow CaNO_3$$

$$CaO + NO \longrightarrow CaNO_2$$

$$CaO + CO_2 \longrightarrow CaCO_3$$

$$CaCO_3 + NO_2 \longrightarrow CaNO_3 + CO_2$$

$$CaO + NO + NO_2 + 3/2\ O_2 \longrightarrow Ca(NO_3)_2$$

Reactions with and absorption of nitrogen oxides were considered as a secondary portion of Phase II investigations. A few references were available for use in the preliminary evaluation of Phase I, but these evaluations had to be made on the basis of some significant assumptions. Since these reactions would affect the character of the desired reactions with SO_x, some knowledge of reactions with other acidic gases was considered necessary. Accordingly each of the candidate systems has received some experimental examination regarding these extraneous reactions.

The reactions of CaO with both CO_2 and NO_2 have been exploited in commercial applications. Although some knowledge of the extent of interferences among SO_2, CO_2 and NO_2 may be available from the experience gained in such practices, there appears to be no reported investigations on the subject.

Nitrogen fixation, as $Ca(NO_3)_2$, has been used in some European countries to supplement natural fertilizers. The usual reaction involves arcing through an air-nitrogen oxide mixture in the presence of MgO or CaO. The reaction efficiencies are too low to consider this as an important reaction in our systems. The prediction of possible reactions such as these within the inorganic liquid salt solvent is difficult, since the solution would already be ionized.

Most of the deleterious SO_2 reactions with molten salt solvents also occur with NO_x. Halides react with both NO and NO_2 to form NOCl, NO or N_2O. Hydroxides also react to form NO, N_2O

and H_2O. The reactions of nitrogen oxides with metal oxides occur in the same manner as SO_2 reactions. The relative acidities and concentrations of the flue gas components will also determine the type and extent of reactions occurring within a stack gas scrubber utilizing a molten salt solvent.

Absorption of NO_x by Molten Salt Candidates

A few screening tests were done to establish the sensitivity of candidate systems towards NO. These tests consisted of fusing the salt mixture under vacuum, adding a small quantity of pure NO, and following the pressure of the system as it was further heated. These data were compared with PVT calculations to note any possible interactions.

The reactions of CaO with NO_x occurred much more rapidly in the KNO_3-$NaNO_3$-$LiNO_3$ eutectic than in $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic. Upon exposure to pure NO, no reaction between NO and CaO was observed in the $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic at temperatures as high as 220°C. A 5 weight percent mixture of CaO in this eutectic was heated in a closed vessel. PVT calculations made on the system agreed with the temperature and pressure measurements made during the test.

When the ternary alkali metal nitrate was used as the solvent, PVT calculations were as much as 25 percent higher than the temperature-pressure measurements made in these tests. Excess water remaining in the salt mixture has been excluded as the source of error in these tests since it has required temperatures in excess of 280°C to remove water from the eutectics.

Substituting BaO for CaO in these mixtures increased the reactivity towards NO_x in both systems. The solubility of BaO in these mixtures is somewhat lower (approximately 1 weight percent as opposed to approximately 5 weight percent for CaO), but the activity towards NO_x was marginally greater.

Combining BaO and $CuSO_4$ in one mixture made the absorption of NO_x promising. Oxidation of NO to NO_2 is increased by the presence of $CuSO_4$ and BaO has been more reactive to NO than CaO. The overall efficiency of the melt decreased, however, due to the formation of sulfite, sulfide and extraneous nitrates, which ruin the eutectic composition.

The reactions noted at the beginning of this section have been studied using both KNO_3-$NaNO_3$-$LiNO_3$ and $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic salt solvents. It was found that nearly quantitative oxidation of NO to NO_2 occurs when 15 percent $CuSO_4$ is dissolved in the nitrate solvent system. Although the reaction of NO with CaO takes place slowly within the nitrate solvent system, NO_2 removal is more rapid and nearly quantitative. The presence of $CuSO_4$ does not change the melting point of the nitrate eutectic; however, copper sulfites, sulfides and nitrates, formed upon exposure to NO-containing gases, increased the melting point severely.

One factor shows up significantly in the examination of each candidate process: the potential is present in each absorption reaction to include the scrubbing of nitrogen oxides. Although the conditions for absorbing the gases are different, it is apparent that the potential exists to remove both SO_x and NO_x from stack gases.

Absorption has been considerably less for NO_x and the economics of NO_x scrubbing would be prohibitive, unless higher concentrations were encountered.

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ABSORPTION PRODUCT ISOLATION

Regeneration schemes proposed for the fused salt systems require the separation of S-containing products from the solvent. The initial product recoveries were made by gravity settling and filtration.

In some cases, a pronounced settling of CaO also occurred with the absorption products. Inconsistent results were obtained with the calcium-sodium-potassium nitrate eutectic, where the solubility of $CaSO_4$ was greatest. Gravity settling was apparently controlled by the size of particles formed during exposure.

Several pore sizes were used for product removal by filtration. No product could be removed by 75 μ stainless steel screens. Complete removal, except for dissolved product, required the use of micrometallic filters, having a pore size of 15 μ.

Neither of these methods could be applied to a large installation where long hold-up times or excessive pressure drops would be prohibitive. After using these techniques to obtain samples for analysis, alternative methods were investigated, which could be incorporated into larger systems.

In the preparation of reaction product samples for TGA studies, several portions of the melt from a run in the stirred reactor were treated with different amounts of water. The melt sample was digested with the desired amount of hot (~90°C) water, filtered and washed with hot water. A three-fold reduction in the amount of water resulted in a slightly better than a three-fold increase in the sulfate content of the water insoluble product.

It appears that about equivalent weights of wash water and total melt will give good product recovery.

Results from the gravity settling tests indicated that it was possible to concentrate the S-containing products by centrifugation. These tests used a standard laboratory centrifuge with no heating, where the sample froze during the settling process. No attempts were made to heat the sample while in the centrifuge, but the melt was heated significantly above the melting point before placing it in the centrifuge. Samples were placed in Pyrex glass tubes, which were subsequently broken and samples taken over the length of the solid salt.

Centrifugation at approximately 3,000 rpm increased the sulfate concentration of the outer segments to more than twice that of the internal segment. Several eutectics were used under similar conditions and all gave some concentration of the sulfur-containing products.

A comparison has been made between the settling rates obtained on two (K-Li)NO_3 eutectics containing 3 weight percent CaO upon standing and being centrifuged. One sample was held in the centrifuge for 10 minutes while the other stood quiescent at 300°F for 30 minutes.

The results from the centrifuged sample showed an increase of approximately 50 percent at the perimeter and a decrease of approximately 67 percent at the vortex from the average sulfur concentration. The sample that was allowed to settle by density differences for three times as long gave an increase of 9 percent at the bottom and a decrease of approximately 3 percent at the top from the average sulfur concentration.

Fused salt solubility measurements indicated that sulfates were less soluble than sulfites for most of these systems. The exceptions were those eutectics containing urea. Since there were some indications that sulfites were the initial product, excess air was added to increase further oxidation.

Three CaO absorption samples were tested for further oxidation upon exposure to air. The total sulfur concentration was compared with sulfur found in the sample after acid dissolution for samples exposed only to the simulated stack gas, stack gas plus one-half as much air and equal quantities of stack gas and air.

The results of these tests showed that further oxidation of the absorption products is minimal under operating conditions. Differences between the sulfate concentrations were near the limits of precision for these analyses. Oxidation of the sample exposed to equal quantities of air and stack gas was small, but definitely greater than experimental error.

Further oxidation of the absorption products does not appear feasible at this operating temperature. The oxidation potential of the nitrate melt is not sufficient to cause further oxidation of the absorption products. The fact that further air oxidation has not been found to occur supports the hypothesis of gas phase interactions over the melt, as observed upon initial exposure.

The overall effects of this phenomenon on the scrubbing system may prove to be desirable, however. The formation of sulfite as the primary produce would decrease the amount of reductant necessary and also improve the water wash separation of sulfur containing products, sulfite being less soluble than the sulfate.

REGENERATION IN MOLTEN SALT SCHEMES

The economic evaluation, performed as a part of Phase I, revealed that the schemes capable of regeneration were the best candidates for treating waste gases from stationary sources. Discarding the "spent" melt or reclamation of the solvent alone cannot be justified when such large quantities are involved.

The sulfur-containing products can be isolated in most of these schemes, for subsequent removal and regeneration. Thermal, chemical and electrolytic methods were described in Phase I, as possible regeneration schemes. More detailed investigations of these candidates have been done during this phase of the program.

General operating and efficiency calculations have removed electrolytic methods as primary regeneration candidates. The energy requirements for these processes are large and an unnecessary burden to stack gas treatment systems since thermal and chemical methods are possible. The final choice of regeneration scheme would be made for a specific installation on the basis of technical, geographic and marketing factors, however.

Thermal Regeneration

The abundance of sulfates and their use as ores has encouraged the investigation and development of many economical methods for their reduction. Preliminary appraisal of thermal regeneration was based on reports by Briner, et al (1949), Cherkov (1960) and Stern and Weise (1966). Thermodynamic calculations were also made using the data of Erdos (1962) for comparison.

Thermal regeneration studies were done in the TGA apparatus shown earlier in Figure 6. Samples of $CaSO_4$, $CaSO_3$, CaS, $Ca(OH)_2$ and $CaCO_3$ were used in this apparatus to measure their decomposition in the pure state, for comparison and correlation.

This investigation was primarily directed towards the examination of reaction products, as obtained from a molten nitrate system containing CaO as the reactive absorbent.

Thermogravimetric analyses were done on water-insoluble samples with the Cahn RG electrobalance. The samples were obtained from KNO_3-$LiNO_3$ eutectic mixtures containing CaO which had been used in absorption studies. A typical data curve is shown in Figure 16, where sample weight is plotted against temperature.

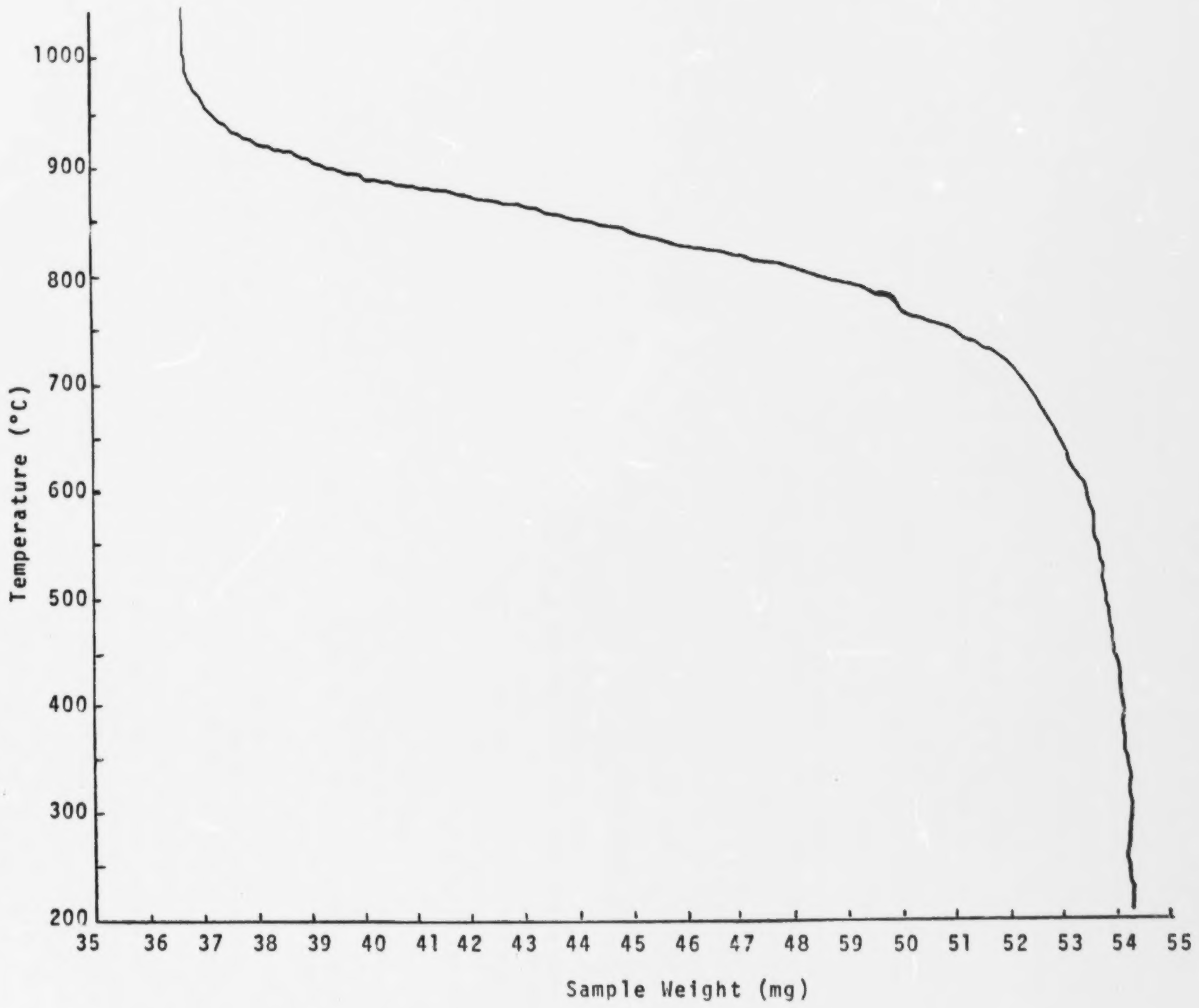

FIGURE 16 - TGA Curve Obtained from Water Insoluble Sample Taken From CaO-Nitrate Eutectic Test

A sample of approximately 100 mg was taken from the water-insoluble portion of salt mixtures and heated at the rate of ten to fifteen degrees Celsius per minute in the TGA apparatus. The weight of the sample was monitored on a strip chart recorder as the millivolt output from the balance.

The TGA curves for the water-insoluble reaction products showed only two significant features: 1) a slow weight loss of from one to five percent between about 150°C and 600°C; 2) a rapid weight loss of from twenty to thirty percent between 650°F and 800°C.

The data from these samples have been compared with similar tests done with the pure salts, mentioned previously, and simulated mixtures. Most of the weight loss observed between 150°C and 600°C can be attributed to dehydration. Only slight discrepancies were noted here, which might indicate the presence of trace amounts of $CaSO_3$.

Although the simulated stack gases contains $\approx$10 percent water vapor, there were no breaks in the temperature curve indicative of $Ca(OH)_2$. The reaction of the acid gas constituents in the stack gases seem to predominate.

TGA curves indicated that the recovered absorption products consisted of CaO, $CaCO_3$ and $CaSO_4$. The proportions of these constituents varied due to differences in the exposure times and methods used to obtain the samples.

In our Phase I evaluation of the CaO-molten nitrate system and in the more recent development of this system, regeneration of the CaO has been considered to be best accomplished by carbothermic reduction of the mixed $CaSO_3$-$CaSO_4$ reaction product to give SO_2 as the intermediate sulfur containing by-product. Several references were found which indicated the feasibility of a slightly different regeneration route.

Reddy et al (1967) have reported on the conditions for reduction of gypsum to CaS by the use of coal. The optimum conditions for reduction are: 1) molar ratio of gypsum to fixed carbon in the coal of 2:1, 2) particle size of both components, 90 percent less than 140 mesh, 3) optimum temperature of 900°C and 4) duration of reaction, 2 hours.

Squires (1969) has patented a process for the reduction of $CaSO_4$ to CaS by CO and H_2 from reformed hydrocarbons. The gas mixture of CO_2 with steam from the reduction is then enriched with CO_2 and used to convert the CaS to H_2S and $CaCO_3$. These data apply to our process, producing H_2S as the intermediate

S-containing product, which could be converted to an elemental sulfur by Claus oxidation. $CaCO_3$ from the steam-CO_2 reaction could then be calcined to give CaO for recycle.

Two experiments were done to evaluate the carbothermic reduction of $CaSO_4$. Synthetic mixtures of carbon (graphite) and $CaSO_4$ were heated in the TGA furnace and the temperature of initial reaction was noted. At a 1:1 mole ratio of C:$CaSO_4$, initial weight loss due to reaction was noted at 820°C. With a slightly higher amount of carbon (C: $CaSO_4$ = 1.2:1), the initial reaction temperature was 800°C.

These tests indicate that the original premise, using carbothermic reduction of sulfate for regeneration, would be feasible for incorporation into large systems. Decomposition of all product species was observed in TGA studies to 820°C, the proposed regeneration temperature. The modifications, mentioned above, would make a product selection available for the individual application, where geographical or marketing location dictated a particularly acceptable recovery product.

Chemical Regeneration

Several regeneration schemes evolved from the literature search of fused salt chemistry. These chemical regeneration methods were based on the acid-base and displacement-type reactions occurring in non-aqueous solvents.

Two candidates were chosen on the basis of theoretical compatibility with the operations of these fused salt scrubbers.

1) A metaphosphate reaction reported by Wrench and Inman (1967) involving acid-base reactions, and

2) A displacement reaction reported by Pechkovskii and Sofranov (1967) and by Duke and Shute (1962).

The metaphosphate reaction is reported as:

$$2\ PO_3^- + SO_4^= \longrightarrow P_4O_7^{4-} + SO_3.$$

Several attempts were made to obtain this reaction with "spent" melts. When the S-containing products were obtained by filtration through a micrometallic filter and treated with metaphosphate, a decrease in the sulfur content was observed.

This test was done in a stainless steel container (Figure 7) under pure nitrogen gas. The SO_2 concentration in the 150 ml/min nitrogen streams never exceeded 500 ppm.

Another test was performed with the entire melt, as it was received from the contactor. After purging the systems with nitrogen, sodium metaphosphate was added to the bubbler. The maximum SO_3 concentration was only 300 ppm in the effluent from this test and nitrogen oxides were released simultaneously.

Analysis of these fused salt mixtures revealed that $Ca(PO_3)_2$ was the major product. It is possible that the NO_x liberated during these tests was the result of subsequent reaction of liberated SO_3 with the nitrate eutectic. The results indicate that this method has limited feasibility in large installations.

Displacement reactions of the type:

$$a)\ SO_4^{=} + C + Cl_2 \longrightarrow 2\ Cl^- + CO + SO_3$$

or

$$b)\ SO_4 + 2\ C + Cl_2 \longrightarrow 2\ Cl^- + 2\ CO_2 + S$$

have been reported to occur in fused chlorides by Johnstone, Darbyshire and Winsche (1942,44). The instability of fused chlorides towards the SO_2 in stack gases limits their use to a separate, regeneration apparatus.

When these reactions were done in nitrate melts the initial reaction appears to proceed as above. After a short period of chloride and SO_3 formation, reactions with the nitrate and halide to produce NO_x and X_2 were observed.

Stable chloride eutectics are limited to a minimum eutectic temperature of approximately 350°C (KCl-LiCl). One test was done with this eutectic with water-insoluble product from an absorption test. The reaction proceeded according to (a) above with the exception that excess chlorine was necessary, which was also found in the effluent. Post-test analysis of the melt also showed that the efficiency of the reaction was limited to approximately 60 percent under these conditions.

The combined reaction of chlorine and carbon does appear to be technically possible. Definition of the reaction parameters and commercial feasibility of the processes necessary for its incorporation into a regenerable, stack gas scrubbing system would require more detailed investigation.

An alternative displacement-type reaction was attempted using transition metal oxides. The solubility of the transition metal sulfates is lower than $CaSO_4$ in these melts. Unfortunately, both the reactivity and solubility of oxides such as MnO, FeO, Fe_2O_3 and PbO was insufficient to cause displacement. Although the transition metal sulfates are better for regeneration schemes, displacement reactions with the $CaSO_x$-absorption compounds does not appear feasible.

ABSORPTION BY COMPLEX-OR ADDUCT-FORMING COMPOUNDS

The more specific tests of Phase II have shown these schemes to be less effective absorbers than indicated in the preliminary screening tests of Phase I. The stability of adduct products and the contactor residence time appear to have a pronounced effect upon the rate and efficiency of absorption. Tests of Phase I candidates, such as $MgSO_4$ and $MgSO_3$, have shown them to be infeasible for even small scrubbers utilizing fused salt solvents under realistic conditions.

Effective absorption rates have been reported for both these compounds in aqueous systems by Pinaev (1963). When used in static or very slowly flowing systems with nonaqueous solvents, similar phenomena have been observed. The effectiveness of these systems decreases rapidly as the gas phase becomes more complex and gas velocity increases.

Tests of the urea-KNO_3-$NaNO_3$ eutectic mixture containing $MgSO_4$ did not reproduce the efficiency of this system noted earlier when contained in the small glass bubblers. Whether the decreased absorption is the result of the contactor design or of slower diffusion within the system has not been established. The stability of adducts formed during this absorption process may also have a significant effect on the absorption efficiency.

Breakthrough occurred almost instantaneously in a mixture containing 0.60 mole $MgSO_4$, with the simultaneous evolution of ammonia. This mixture, if it had reacted as in previous screening tests, should have scrubbed the stack gas for a period of several hours. Sulfur dioxide appeared to react preferentially with the urea rather than with the magnesium compounds in the larger bubblers.

Mixtures (50-50 weight) of $MgSO_4$ with $MgSO_3$ and Na_2SO_3 were added to the urea KNO_3-$NaNO_3$ eutectic to improve absorption within the melt. The results of a representative bubbler test are plotted in Figure 17. Although such mixtures have been reported by Pinaev (1968) to have good absorptive properties in aqueous solutions, the non-aqueous fused salt systems have failed to realize this high absorptive capacity.

When the stack gas flow was increased through the system to give a residence time of less than 10 seconds, absorption was minimal. Several other sulfates were used which were reported by Lundquist (1963) to be reactive with SO_2. Those sulfates which have dissolved have done so only sparingly in the urea-KNO_3-NaNO eutectic. The presence of SO_x within these mixtures has resulted in the release of ammonia. It is possible to

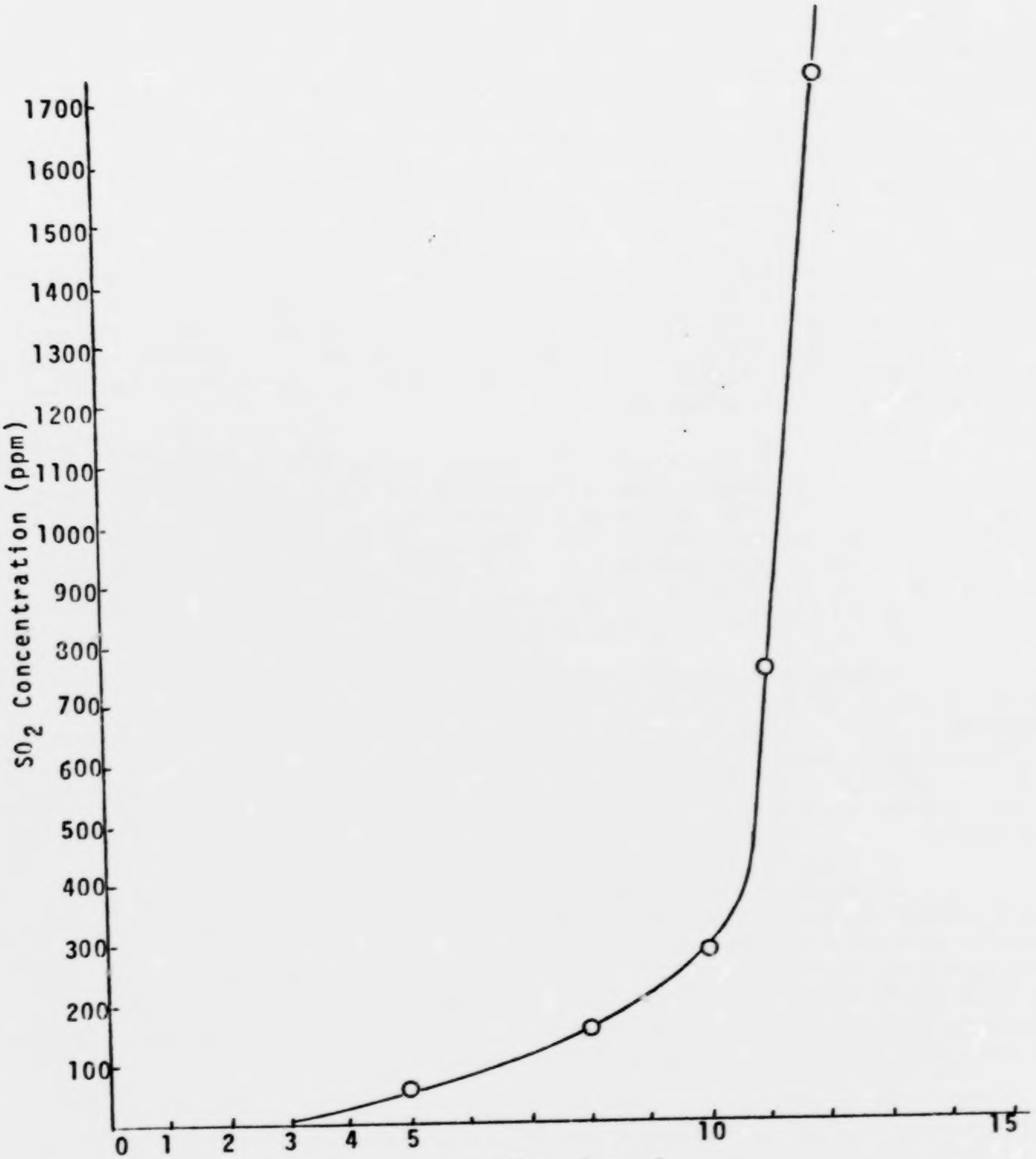

FIGURE 17 - Effluent SO_2 Concentration From Bubbler Containing 20 wt/o $MgSO_4$ and 20 wt/o Na_2SO_3 in Urea-KNO_3- $NaNO_3$ Eutectic

partially reduce these undesirable reactions by operating in the temperature range 200-230°F with a maximum of the adduct forming compound present; but they are not completely removed.

It was found that some oxidation of SO_2 to SO_3 occurred at the elevated temperatures occurring in non-aqueous solvents. The results of these tests are shown in Table VI, where it may be seen that absorption, by way of adduct formation, does not appear feasible.

Reactions of CO_2 and NO with adduct forming species were also minimal. These reactions have been found to follow the acidic nature of the gases (i.e., with SO_2 much more reactive than the others). The SO_2 adducts have been found to be unstable in fused salt solvents and adducts of the other acid gases are correspondingly less stable.

Tests with the urea-KNO_3-$NaNO_3$ eutectic containing $MgSO_4$ have shown that there is little or no adduct formation with NO. Although NO absorption in aqueous systems is reported by Hollander and Kerenyi (1966), it was not observed in non-aqueous systems. It is most probable that NO does not enter into the reaction scheme in the nitrate melts due to their oxidizing properties. Adducts with the NO_2 group have not been found for magnesium compounds. It appears that separate reactive species may be added to this solvent which are more specific for NO or SO_2. At the present time no candidates are known which would form adducts with both nitrogen and sulfur oxides and yet be stable towards the stack gas.

The insertion of NO into ferrous compounds is common in many analytical schemes because of its coloration and quantitative reaction. Some of the adduct-forming reactions reported for aqueous systems occurred when the urea-alkali nitrate eutectics are employed as solvents. Although no references have been found for $MgSO_4$, iron, nickel, chromium and manganese sulfates are reported to form adducts of the type $FeSO_4 \cdot NO$. Information on the stability of the products and the rates of formation is not available. These tests indicate that the reactivity of SO_x is greater and that SO_x adducts are preferred even to the point of replacing NO from complexes.

The general conclusion to be drawn from this information is that SO_x absorption predominates over NO_x in stack gases containing sulfur oxides, but even this absorption is minimal.

Additions of Mn Compounds to the Nitrate Solvent

Brough, Habboush and Kerridge (1968) have reported the solubility and reactions of MnO_2 in fused nitrates. Without pyrosulfate or other promoters in the melt, we have not observed

TABLE VI - COMPLEX-FORMING COMPOUNDS AS SO_2 ABSORBERS

Complex-Forming Compounds	Solvents	Bubbler Absorption Characteristics
1. $MgSO_4$	Urea-KNO_3-$NaNO_3$	good in near static systems; poor with practical stack gas flow
	KNO_3-$NaNO_3$-$LiNO_3$	insoluble
	$Ca(NO_3)_2$-KNO_3-$NaNO_3$	insoluble
2. Na_2SO_4	Urea-KNO_3-$NaNO_3$	poor; release of NH_3 almost after exposure
	$Ca(NO_3)_2$-KNO_3-$NaNO_3$	insoluble
	$LiNO_3$-KNO_3-$NaNO_3$	insoluble
3. $MnSO_4$	Urea-KNO_3-$NaNO_3$	negligible absorption; some NH_3 released with SO_x
	KNO_3-$NaNO_3$-$LiNO_3$	poor solubility; immediate release of NO_x upon exposure
4. $BaCaO_4$	Urea-KNO_3-$NaNO_3$	poor solubility, NH_3 released from melt soon after exposure
	KNO_3-$NaNO_3$-$LiNO_3$	slight absorption followed by release of SO_x-NO_x
	KNO_3-$NaNO_3$-$Ca(NO_3)_2$	slight absorption followed by release of SO_x-NO_x
5. $Ca_3(PO_4)_2$	KNO_3-$NaNO_3$-$LiNO_3$	short absorption period followed by release of SO_x-NO_x
	$Ca(NO_3)_2$-KNO_3-$NaNO_3$	short absorption period followed by release of SO_x-NO_x
	Urea-KNO_3-$NaNO_3$	poor solubility, both NO_x and NH_3 released from melt
6. $Mg_3(PO_4)_2$	Urea-KNO_3-$NaNO_3$	poor solubility;
	KNO_3-$NaNO_3$-$LiNO_3$	insoluble
7. $NiCl_2$	Urea-KNO_3-$NaNO_3$	poor solubility; both Cl_2 and NH_3 released upon exposure to stack gases

the reactions reported in their work. MnO_2 is nearly insoluble in the alkali metal nitrate eutectics, but forms a suspension in the $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic.

It was found that the reaction between $KMnO_4$ and NO_x,

$$KMnO_4 + NO \xrightarrow{\text{basic}} KNO_3 + MnO_2,$$

would take place in the nitrate solvent. The presence of approximately 10 weight percent $KMnO_4$ in the melt does not significantly change the stability of the melt in the 130-180°C operating range. The reaction forming MnO_2 proved to be quite detrimental in the operation of the small bubblers used for experimental screening. MnO_2 is reported to react with SO_2 according to the reaction:

$$MnO_2 + SO_2 \longrightarrow MnSO_4.$$

If this reaction could be maintained in a system operating with a stack gas composition, the total build-up of MnO_2 would be minimal. It appeared to be completely overshadowed by the CaO reaction, however, allowing the MnO_2 precipitate to increase and plug the scrubber. A 5 weight percent suspension of MnO_2 in $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic did not absorb SO_2 from a simulated stack gas with any efficiency. As plotted in Figure 18, as effluent SO_2 concentration in ppm versus time, absorption was fairly good during the first 15 minutes of exposure; the SO_2 concentration in the effluent gas stream begins to increase almost linearly from this point on.

Analysis of the spent melt failed to identify $MnSO_4$ in any portion of the system. A maximum of approximately 7.5 percent of the MnO_2 concentration would have been used for the quantitative reaction with SO_2 in this test. Semi-quantitative analyses indicated less than 1 percent of the MnO_2 was used in absorption reaction, none of which formed the sulfate.

A 7 weight percent suspension of $KMnO_4$ in $Ca(NO_3)_2$-KNO_3-$NaNO_3$ eutectic absorbed the SO_2 concentration from a stack gas better than the MnO_2-containing melt. As seen in Figure 18, no SO_2 was measured in the effluent gas stream during the first 5 minutes of operation. There was more interference from the nitrate solvent reaction in this test, however. NO_2 was observed only in the first few minutes of operation in the test with MnO_2. When $KMnO_4$ was used as the reactive species, NO_x came off at a rate of a few ppm throughout the test.

MnO_2 is formed during the absorption; possibly through reactions such as reported by Kerridge and Tarrig (1968) and Bennett and Holmes (1962):

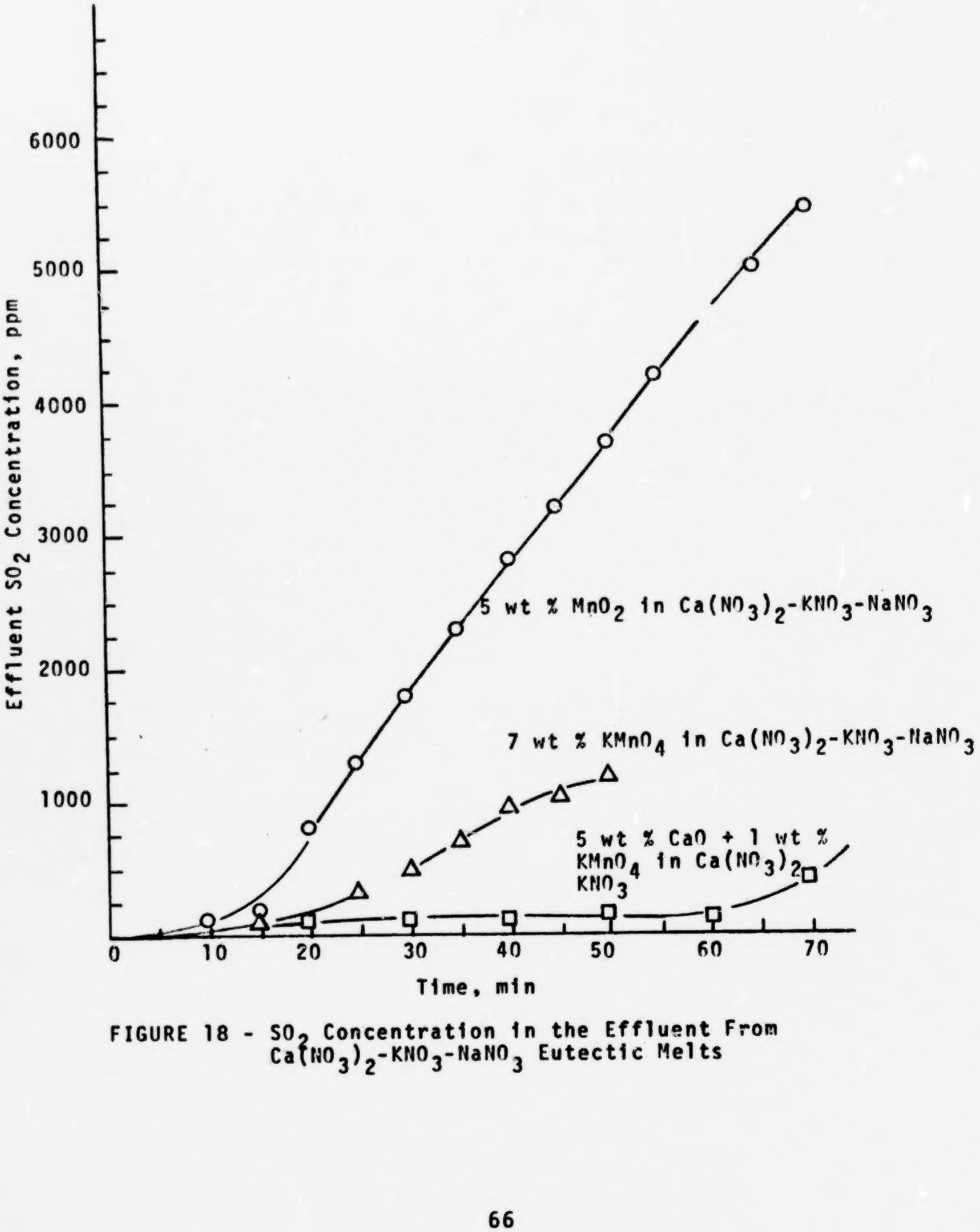

FIGURE 18 - SO_2 Concentration in the Effluent From $Ca(NO_3)_2$-KNO_3-$NaNO_3$ Eutectic Melts

(1) $2\ MnO_4 + SO_2 \longrightarrow 2\ MnO_2 + SO_4^{=} + O_2$

(2) $MnO_4^- + NO \longrightarrow NO_3^- + MnO_2$

(3) $4\ MnO_4^- + 2\ NO_3^- \longrightarrow 4\ MnO_4^{=} + 2\ NO_2$

(4) $2\ MnO_4 \longrightarrow 2\ MnO_2 + 2\ O^{=} + O_2$

(5) $MnO_4^{=} \longrightarrow MnO_2 + O_2^{=}$

(6) $2\ MnO_4^{=} + 2\ NO_2^+ \longrightarrow 2\ MnO_2 + 2\ NO_3^- + O_2$

taking place in fused nitrate mixtures containing permanganates. The overall reaction depends upon the concentration of reducible species in the melt. The oxygen absorbed from the flue gas appears to be sufficient to maintain these reactions at a nominal rate. The overall reaction becomes therefore:

$$4\ MnO_4^- \longrightarrow 4\ MnO_2 + 2\ O^{=} + 3\ O_2$$

with the oxide immediately reacting with CO_2 or SO_2 available in the stack gas.

Approximately 3 weight percent of the MnO_4^- was reacted to form MnO_2 and precipitated from the fused salt. Filtering the solution from the bubbler removed all but approximately 0.5 weight percent of the sulfur-containing species from the nitrate solvent. The total absorption of sulfur was small and these measurements were made near the limits of the analytical methods.

The permanganate reaction proved much better for SO_2 absorption and was combined with CaO in one test. The first preparation of the melt was unsuccessful due to interaction of the CaO, $KMnO_4$, nitrates and water combined in the melt. Dehumidifying and adding the reactive components separately resolved this problem.

A plot of the SO_2 concentration in the effluent gas from this melt is also presented in Figure 18. This test was done with a simulated stack gas containing 8,700 ppm SO_2 to which 2,000 ppm NO was added before humidification. No interferences were noted, although several hundred ppm NO passed through the bubbler during the test.

MnO_2 was found in all parts of the system. No attempts were made to filter the melt since its viscosity increased considerably throughout the test. The $KMnO_4$ color was bleached from the upper portions of the melt and replaced by that of MnO_2. Only traces of sulfate were found in this portion of the melt. A precipitate, forming at the bottom of the glass container, contained the sulfate formed during the test. None of the sulfate formed was water soluble, indicating little or no reaction with manganese. Although MnO_2 has been reported by Beinstock, et al, (1961) to react with SO_2 according to the reaction,

$$MnO_2 + SO_2 \longrightarrow MnSO_4,$$

we have been unable to attain this reaction in a fused salt where the MnO_2 is insoluble in the reaction media.

"IN SITU" TRANSITION METAL OXIDE SYNTHESIS

Oxide ion donors were the most promising reacting species for the chemical absorption of SO_2 from stack gases. CaO has been the best candidate from absorption data, but it lacks the easy regeneration common to almost all the transition metal sulfites and sulfates.

Transition metal oxides are all insoluble in the nitrate eutectics used as solvents for these scrubbing systems. To circumvent this problem, several methods were attempted to dissolve transition metal oxides into nitrate-compatible, or other nitrate-containing eutectics. Most oxides have a measurable solubility in molten halides, and the halides form eutectics with nitrates. These systems are doubly sensitive towards SO_2, however, since both the halide and the nitrate react and oxide ion catalyzes the halide reaction.

Colloidal dispersions were made in the $(Ca\text{-}K\text{-}Na)NO_3$ eutectic since it has the highest viscosity. It has also displayed better solvent characteristics towards oxides and sulfates. Bubblers depending on this solid gas contact for absorption had a very poor efficiency and, in most cases, what product was formed was also soluble or suspended in the solvent.

Decomposition and displacement reactions were used with the transition metal nitrate eutectics, with some depressing the freezing point of the eutectic as much as 10°C. The instability of transition metal nitrates and the tremendous oxidation potential of the alkali nitrate eutectics usually sufficed for decomposition of the transition metal compound to its oxides. Where these two driving forces were not sufficient, CaO was added to the melt, causing a displacement reaction.

Using the above techniques, suspensions of Pb, Cu, Co, Ni, Al, Ti, Cd, Zn, Fe, Ba and Mn oxides were formed "in-situ" in the alkali nitrate eutectics and the urea-$(K\text{-}Na)NO_3$ eutectic. Ba, Cd, Cu and Ti were the only metals to form large oxide crystals which settled out quickly. Even with these metals, a portion of the oxide remained, as with all the other metals tried, in suspension for approximately one hour.

None of the transition metal oxides was as basic as CaO, allowing the nitrate reaction to evolve almost equal amounts of NO_2 and SO_2 into the effluent gas stream. Zn, Fe and Cu were the most promising candidates, but ZnO also absorbed CO_2 to form the less reactive carbonate so that the NO_2 concentration in the effluent was constantly increasing.

The results of these tests (Figure 19) indicate that it is useless to attempt these reactions in the inorganic fused salt candidates we have found compatible with simulated stack gases.

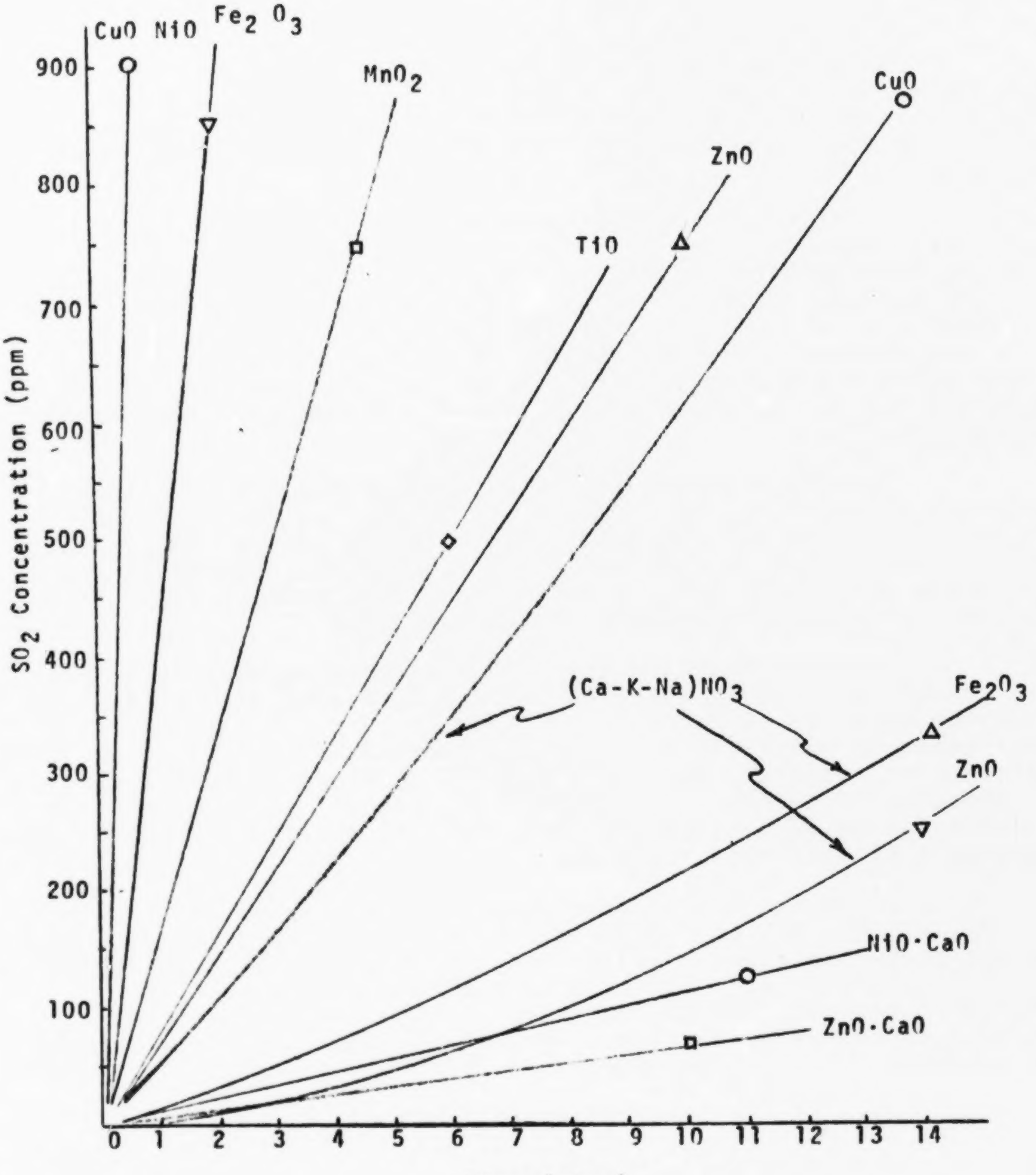

FIGURE 19 - Effluent SO_2 Concentration from Bubbler Containing Transition Metal Oxides Suspended in (Li-Na-K) NO_3 Eutectic

LIQUID METAL SYSTEMS

Liquid metal alloy systems were chosen as candidate SO_2-scrubbers on the basis of five theoretical advantages:

1) Alloys are available which are liquid at stack gas temperatures and will react with the acid gases.

2) Metal systems contained the highest concentrations of SO_2-reactive species and offered good "loading factors".

3) Large density differences between carrier and product assure the separation of products in concentrated form for regeneration.

4) In contrast to the more modern developments in fused salt processes, the metallurgical reactions occurring in these schemes have been known and studied for years.

5) Both separation and regeneration of metal systems appear straightforward and economical.

Of the considerable number of metal alloys having melting points in the desired range, the results of Phase I studies limited the candidates for the experimental work of Phase II to the Sn-Pb-based alloys. The majority of the white metals were found to be too reactive, undergoing deleterious reactions upon exposure to stack gases. Specifically, oxidation was the most serious interference, since the oxides formed are solids and react slowly with gas-solid contact. Since oxygen is usually present in stack gases at many times the SO_2 concentration and regeneration of metal systems requires equal amounts of reductant for both oxides and sulfur-containing species, the costs of operation are directly proportional to the amount of oxidation.

Reaction Chemistry

Thermodynamic calculations of the metal alloy systems, done in Phase I, indicated that a dross of oxide-sulfate-sulfite-sulfide product should be formed upon exposure to the simulated stack gas which would float on the surface of the pool of metal. Lead was the most reactive component according to these calculations. The complexity of the stack gas permitted many interfering reactions which could not be calculated, however.

Reactions with some of the other constituents of stack gases were thought to be desirable. The most important of these was the possible absorption-reaction of nitrogen oxides. Many of the earliest chemists (J.L. Gay Lussac, J. Dalton, E. Muller, J. Priestly, P. Sabatier and H. Davy) investigated the reactions of various metals and their oxides with NO. The reactions of Sn and Pb to form oxides are only two examples of a rather large group including Fe, V, Al, Co and Cr. It is, in part, propitious that most of these metals are also reactive towards sulfur oxides. With the liquid metal absorption scheme, there is a large excess of reactant which would be available for scrubbing both NO_x and SO_x.

The variety of reactions possible in the molten metal system is large. No attempts were made during the performance of Phase I studies to make exhaustive chemical or rate measuremeans on the candidate reactions. Tests of Phase II were designed to examine some of the possible reactions occurring within the absorption unit; to identify the products; and determine if there were deleterious side reactions.

NO_x Absorption

Some work has been reported regarding the activity of lead and tin towards other acid gases. The Pb-Sn system has received more attention in this area than the other candidate systems since the catalytic behavior of Pb is used in the Lead Chamber process for the production of H_2SO_4. Although this process has a long history, there is some ambiguity concerning the exact nature of the reaction mechanisms. The general reactions:

$$NO_2 + SO_2 + H_2O \longrightarrow NO + H_2SO_4$$

$$NO + NO_2 \longrightarrow N_2O_3$$

$$N_2O_3 + 2\ H_2SO_4 \longrightarrow H_2O + 2\ HONSO_4 \text{ (and others)}$$

are proposed to explain the final product. Nevertheless, the process and its modifications are well established.

In addition to this catalytic reaction, lead and tin oxides also react with both NO_2 and NO to form nitrates, nitrites, oxides and N_2O. Oxide reactions have appeared to predominate in the absorption of SO_2 from flue gases. The extent to which these competitive reactions might interfere or synergize one another cannot be easily calculated, and no reports were found concerning the reactions of mixtures containing oxides of both sulfur and nitrogen.

Experimental

Screening tests and further evaluation of the Sn-Pb alloys and modifications were performed in a stainless steel bubbler apparatus shown in Figure 20. This apparatus, which had a stainless steel blade stirrer, was used to measure various degrees of agitation from surface rippling to the centrifugal spraying of droplets, similar to that used in the fused salt contactor.

Density of the liquid metals was a formidable detriment in simple bubbler tests. Only the lowest flows could be scrubbed with any efficiency as the gas bubbles congealed in the melt and restricted contact area to the extent that little or no absorption was observed.

The Effect of NO in Simulated Stack Gas on the Sn-Pb Alloy

A test of the Sn-Pb eutectic alloy was conducted at 420°F with the simulated smelter gas (3.8 percent SO_2) containing 2,000 ppm NO.

Poor absorption characteristics were attributed to insufficient agitation of the melt and lower contact or residence time within the absorbing medium. The gas residence time was approximately 1 second in this test, while it varied between 2 and 3.5 seconds in the apparatus used for previous tests.

The presence of NO also appeared to increase the extent of oxidation of the alloy melt. Samples of the material floating on the surface of the melt contained 85-90 percent metal; most of the samples varied somewhat in composition, but both Sn(II) and Sn(IV) were present in nearly equal quantities. Only a trace of PbO was found and it appeared that most of the sulfur had been reacted to form SnS.

The NO reaction should result in the formation of oxides or nitrates under these conditions, but there were no traces of nitrate obtained in the samples from this test. The increased oxidation may be attributed to absorption of NO from the stack gas and any nitrate formed would react with SO_2 to form the sulfate and release NO_2. The chemical bubbler used to detect nitrogen oxides did not indicate their presence during the first nine minutes of operation. After this breakthrough had occurred, it was impossible to absorb all the NO from the gas stream even when its concentration was decreased to approximately 800 ppm.

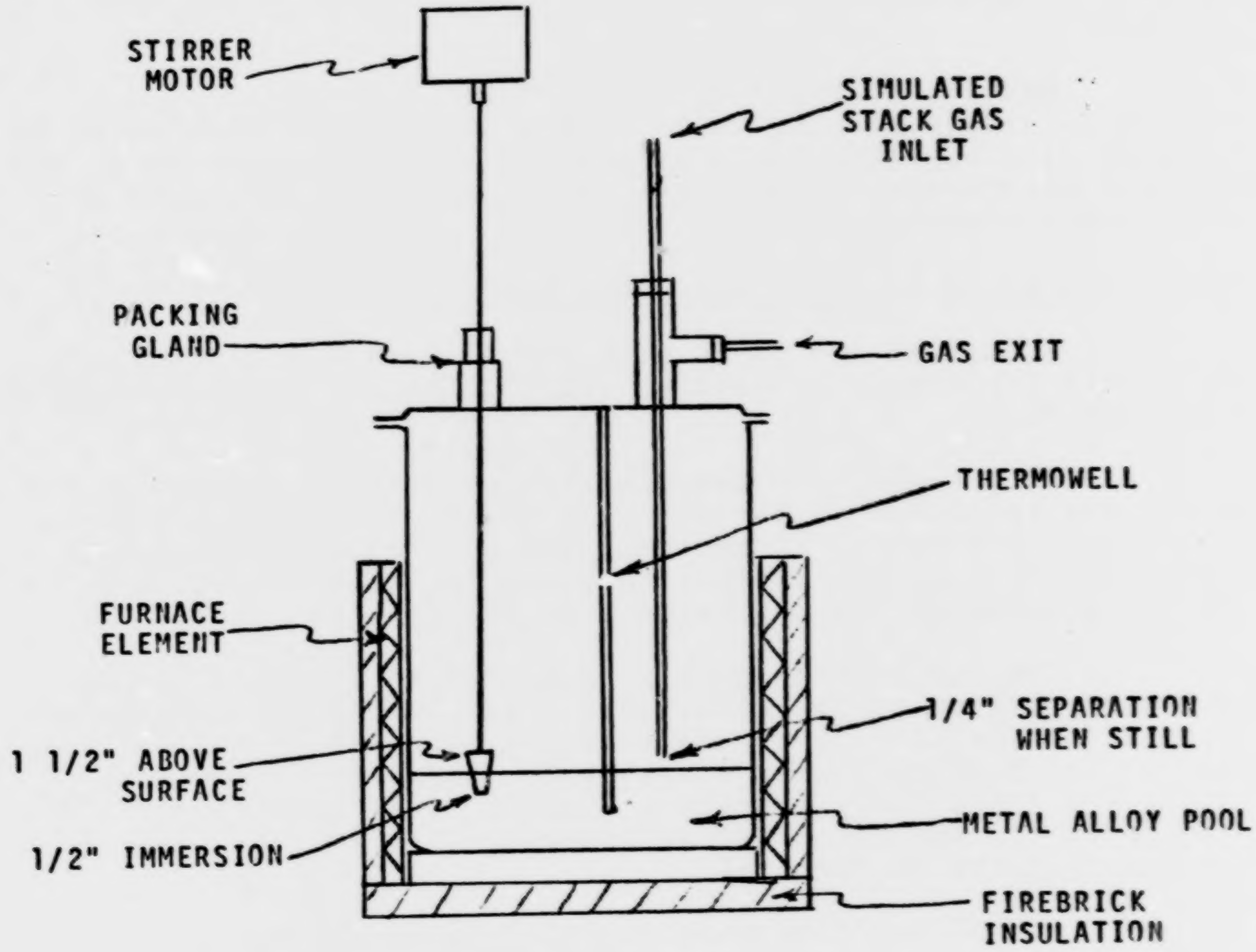
STIRRER MOTOR
SIMULATED STACK GAS INLET
PACKING GLAND
GAS EXIT
THERMOWELL
FURNACE ELEMENT
1/4" SEPARATION WHEN STILL
1 1/2" ABOVE SURFACE
METAL ALLOY POOL
1/2" IMMERSION
FIREBRICK INSULATION

FIGURE 20 - Stirred Reactor for Molten Metal System

Sn-Pb Eutectic Alloy Tests

Analyses of SO_2-absorption tests using the Sn-Pb eutectic alloy indicated that oxidation was the first step in absorption. Sulfurization must proceed apace with oxidation if the process is to be economically regenerable. In every case, however, the concentration of oxides was approximately double that of the sulfur-containing species.

The total absorption capacity of these alloy systems was small in proportion to their potential. Thermal gradients within the system and splashing of the alloy under agitation were considered the major factors contributing to their limited capacity. As the metals entered cooler portions of the bubbler they solidified and were lost for further reactions. The absorption capacity could be increased considerably by operating in an isothermal system or one which had no part lower than the freezing point of the alloy.

These more detailed tests of the absorption characteristics of the metal systems confirmed the need for a third component in the Sn-Pb system, to provide oxidation resistance. A test of the binary eutectic alloy during which the metal was stirred at approximately 1,000 rpm revealed that better contacting would help SO_2 scrubbing, but it also permitted more oxidation.

Since Sn is the more oxygen-reactive metal in the candidate eutectic alloy, pure Pb was used in the bubbler apparatus as a base line test. Absorption of SO_2 was almost negligible. The best absorption efficiency, approximately 50% removal, was observed during the first four minutes of operation. The concentration of SO_2 in the effluent gas stream then increased exponentially towards that of the delivered gas.

The oxidation rate of Pb was decreased by a small addition of Sn. This rate, at the higher temperatures necessary for operation ($\approx$650°F), does not differ significantly from that of the eutectic operating at 400°F. The most encouraging methods of treating this problem area appeared to be through the use of one of the transition metals in a eutectic alloy.

White metal alloys having a lower melting point than the Sn-Pb eutectic were rejected through a number of problem areas. Ternary, or higher, alloy systems would require significantly more surveillance to maintain proper concentrations. Additionally, most of the low-melting components had greater susceptibility towards oxidation than the Sn-Pb system.

Ternary Alloys

The oxidation resistance of the Sn-Pb eutectic was increased by adding 0.02 percent Al according to the report by Kubaschewski (1962). The aluminum was added to the molten eutectic at 450°F with stirring. Oxidation of the surface of the melt, which had occurred at a rate similar to that observed in other preparations of the eutectic alloy, was stopped. The majority of the aluminum added to the eutectic alloy was found to be on the surface. The melt did, however, retain most of its oxidation resistance. The melting point of this ternary mixture was 360°F.

This Al-containing alloy showed no capabilities towards absorbing SO_2 from a simulated stack gas. Although the surface of the melt had a similar physical appearance to previous tests, no sulfate was present. A trace of sulfide was the only identifiable sulfur-containing species. Oxides were, again, the predominant species, with Al_2O_3 the major component. The absorption characteristics of the Al-inhibited Sn-Pb alloy confirmed it was possible to inhibit the oxidation of the Sn-Pb alloy upon exposure to stack gas.

Nitric oxide was added to the stack gas later and was absorbed in this melt, probably according to the reactions:

$$Sn + 2\ NO \longrightarrow SnO_2 + N_2$$

or

$$Pb + NO \longrightarrow PbO + 1/2\ N_2$$

The formation of oxides, by these reactions, increased the absorption of sulfur dioxide slightly. Nitrogen oxides were identified in the effluent gas stream, however, after 5 minutes operation in a stack gas containing approximately 6,000 ppm NO.

Both Zn and Cu were also reported by Kubaschewski (1962) to have inhibitive effects significantly less than Al. A ternary eutectic of Sn-Pb and Zn was prepared for use as an SO_2 scrubbing medium. The eutectic had a melting point of about 330°F, which was a slight improvement over the 362°F melting point of the binary eutectic. The approximate eutectic composition was 64 Sn - 29 Pb - 7 Zn.

It was necessary to use an inert gas cover during the initial melting and preparation of these alloys, to avoid excess oxidation before the slow dissolution of Zn was completed. The metals were heated in excess of 300°C for nearly an hour during eutectic formation. Either argon or N_2 was used as the cover gas for these operations.

Investigation of the Sn-Pb-Zn system included examining both the physical characteristics of the ternary alloy and its capabilities as a stack gas scrubber. Rough solubility and melting point determinations were made to supply better means of identifying the alloys. Maximum Zn solubility was found to be in the range 8-10 weight percent, with dissolution being rather difficult. The melting point decreased almost linearly with the

Zn concentration to a minimum of 170-175°C. These are somewhat different than the values published by Mathewson (1959), in which the ternary eutectic melts at 177°C and contains approximately 4 weight percent. The ternary alloy does, however, offer a lower operating temperature and greater oxidation resistance than the binary eutectic of Sn-Pb. Negligible oxidation was observed at temperatures as high as 220°C (430°F).

Variations in the physical and chemical properties of the Sn-Pb-Zn alloy were observed as the concentration of Zn was changed. Analysis of the melt from an alloy containing 5 weight percent Zn revealed that most of the chemical reactivity rests in the Zn. Small amounts of lead and tin oxides were found in the dross, which also gave an inconclusive test for $Sn(SO_4)_2$. Both sulfurization and oxidation occurred through the Zn.

After this data had been obtained from a system containing "excess" Zn, further tests were made to evaluate the use of Zn as the reactive species with the Sn-Pb eutectic acting as the solvent carrier. This would have proved advantageous for both absorption and regeneration. The possibilities of Zn compounds as SO_2 absorbers have been reported by Poisakhov and Krylov (1963). The results of two tests were sufficient to show that a predominant Zn-reaction could not be obtained with workable alloys.

Experimental work with the molten metal systems then concentrated on the ternary system of Sn-Pb-Zn, where the composition ranges included 55 to 86 weight percent Sn, 10 to 37 weight percent Pb and 0.1 to 10 weight percent Zn. These systems were studied to determine the composition displaying the best compromise between SO_2 absorption and oxidation resistance. Increasing the oxidation resistance of the alloy always resulted in a simultaneous decrease in reactivity towards SO_2. The alloy composition range of approximately one weight percent Zn in the Sn-Pb eutectic had the best compromise in reactivity for unstirred contactors.

A problem of phase separation occurred when this new alloy was used in a stirred reactor, however. Both Hansen (1958) and Mathewson (1959) report the existence of two liquid phases in these alloys. Formation of this separate phase occurred only in tests where a stirrer was used to agitate the liquid. For these systems it was necessary to use the alloy containing approximately 0.5 weight percent Zn.

Separation of this "intermetallic" phase is difficult to explain. The fact that it was preferably formed by stirring the alloy could be explained by simple association of the components during agitation. The reactivity of Sn towards the stack gas and towards sulfur-containing products of the other metals also could promote this separation. Another explanation, which could not be corroborated by analysis, is the formation of plumbates or zincates.

Phase separation, due to the formation of an intermetallic, was a problem in all stirred Zn-ternary systems containing more than 1 weight percent Zn. Each test in which an alloy containing >1 weight percent Zn was used experienced some phase separation. The extent and nature of this separation or stratification appeared to depend on the Zn concentration, amount of agitation and the extent of oxidation occurring during the test. The result was the formation of a pasty, viscous mixture with much higher liquefaction temperature. Phase separation in alloys containing <1 weight percent Zn was less and included a higher sulfur concentration.

This stratification would be advantageous if it was the result of SO_2 absorption and formation of some sulfur-containing compound. There is a small amount of sulfur (as sulfide) in the dross, but when the Zn concentration exceeds 1 weight percent, the majority of the dross contains a Pb-Zn intermetallic.

The non-metallic components of the dross are oxides and sulfides of zinc and tin. SnS appears to be the primary sulfur-containing compound, but there is some evidence for the formation of zincates. We could not make a positive identification of zincates, but the complexity of the dross indicated some interaction of this type.

The data presented in Figure 21 was taken from a test in which an alloy containing 67.5 weight percent Sn, 30.8 weight percent Pb and 1.7 weight percent Zn was exposed to a simulated stack gas containing a nominal 3.2 percent SO_2. Several tests such as this indicated that contact surface area, and the type of contactor used, are critical factors in absorption and efficiency of the molten metal systems. A comparable alloy mixture was used in the unstirred test which is shown as a comparison in Figure 21.

Analysis and Chemical Reactivity of Metal Systems

Analyses of the alloys reveal little effect of absorption upon the metal concentrations of the major portion of the melt. The metal concentrations measured in the surface material, a scum of reaction products, have varied considerably with different alloys and operating procedures. The Zn concentration increased on the surface and both Zn and Pb decreased. The ratio of Sn to Pb also increased, since Sn was the more reactive. Oxides of all the components were found, as well as both Zn and Sn sulfides. There was no evidence of the formation of SnO_2 in tests where Zn was present. In previous tests, in which no oxidation depressant was included, most of the oxidation occurred through the formation of SnO_2.

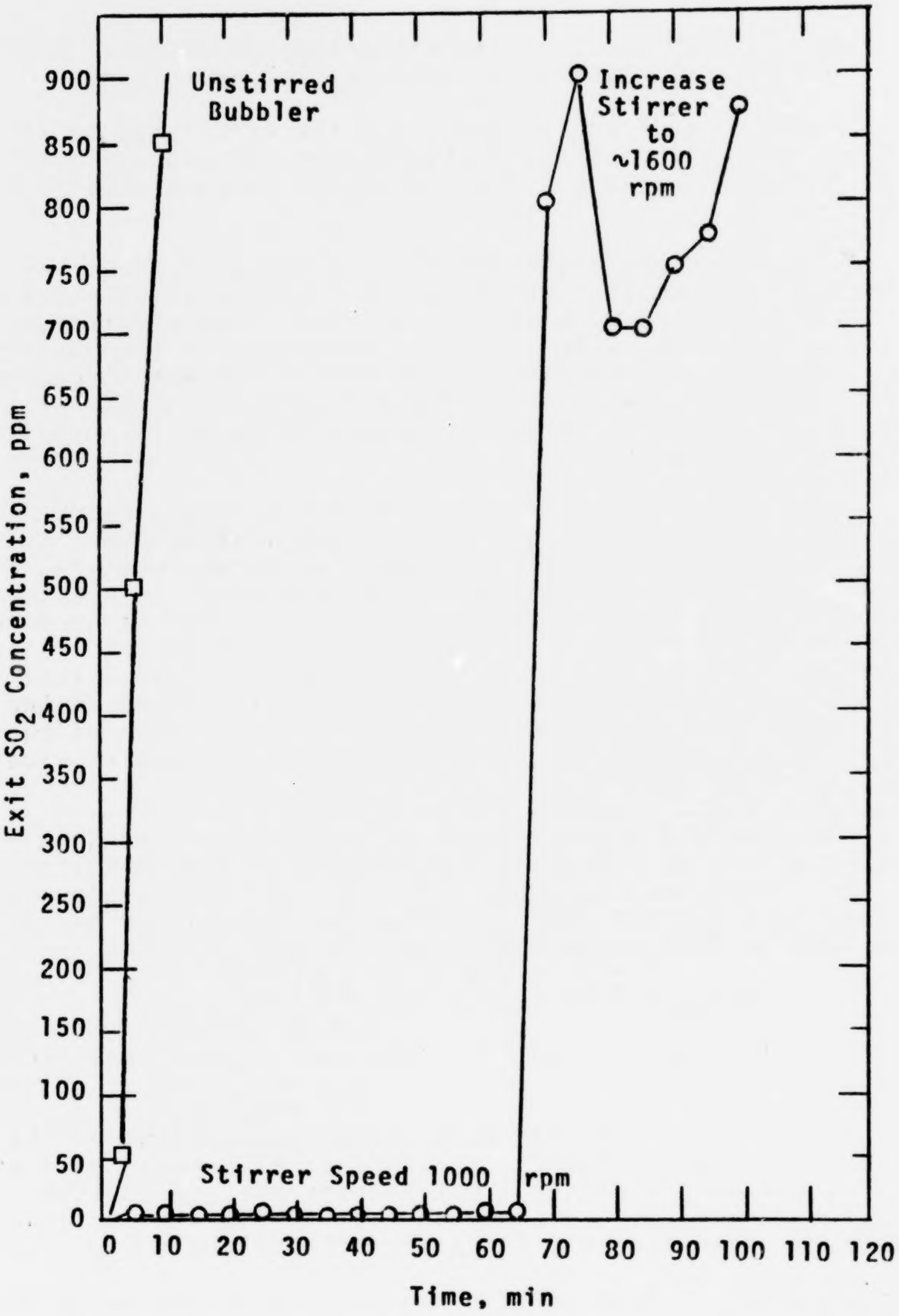

FIGURE 21 - Absorption of SO_2 From 3.2% SO_2 Smelter Gas by Sn-Pb-Zn Alloy

The primary S-containing absorption products of the ternary alloy Sn-Pb-Zn have been characterized as sulfides.

The nature of the products and the efficiency of absorption was not appreciably affected by the addition of an oxidation inhibitor but the surface scum was concentrated in sulfides.

Some oxidation of Sn and Pb occurred when the Zn concentration is reduced to 1 weight percent or lower for those tests in which the ternary alloy was stirred. The absorption efficiency was affected only slightly, however, and the amount of oxide formed was not excessive. Oxidation has been shown to be the necessary, initial step in SO_2 absorption and only becomes detrimental when an excessive amount of oxide is delivered into the regeneration cycle.

Both Sn and Zn sulfides are formed during exposure to the simulated stack gases. SnS predominates with exposure to flue gas concentrations but ZnS increased in those tests in which a simulated smelter gas concentration was employed. Since the SO_2-reactivity of these alloy systems has been shown to be oxygen dependent, it appears that the initial absorption occurs via the oxides and SO_2. We have shown, in small crucible tests, that the sulfates are unstable in the Sn-Pb alloy, being reduced to the sulfides. This internal oxidation may account for some of the problems encountered with these systems concerning their oxidation potential.

The internal oxidation of the metal should have an accelerating effect on the absorption of SO_2 by the formation of oxides. The indications are that suboxides, or dissolved oxygen, are the promoters for the SO_2-absorption and that gross oxide formation such as that occurring by way of the reaction

$$Sn(SO_4)_2 + 5\ Sn \longrightarrow 2\ SnS + 4\ SnO_2$$

results in the formation of solid oxides, which have considerably slower reactions with SO_2.

Tin appears to be the most reactive component of the alloy. Oxidation is limited to tin and zinc oxides and most of the sulfur-containing products are tin compounds. A smaller concentration of PbS was formed concurrently with similar concentrations to those obtained in unstirred bubblers.

A sample of lead sulfate was fused with the Sn-Pb eutectic at 400°F to determine the extent of interaction. Lead sulfate was reduced in the presence of the molten eutectic alloy with the formation of SnS, SnO_2 and PbO, leaving some lead sulfide. In contrast to the samples taken from the Sn-Pb eutectic exposed to simulated flue gas, the non-metallic-appearing samples from this melt contained a trace of sulfide along with some sulfate. Samples taken from the absorption unit contained only trace amounts of sulfate.

Analyses performed on these tests established some patterns. Metal samples taken from various positions in the system showed variations in the alloy constituents. These metal analyses indicated that alloys containing 0.5 weight percent Zn remain liquid throughout the tests. Samples of the splashed alloy and the liquid remaining after a test agree in all metal concentrations. A typical analysis is presented, along with the position of the samples, in Table VII.

Samples taken from the top of the melt varied according to the reactions occurring during the test. For those tests in which absorption proceeded well, the Sn content of the dross increased, ostensible by the SnS-containing compounds. When the Zn concentration in the alloy was high,absorption was less and the concentration of Pb increased significantly in the dross. This was attributed to the formation of Pb-Zn intermetallic phases, whose melting points are considerably higher.

All the sulfur retained in the liquid metal scrubber appears to be present as sulfide. The presence of Zn apparently removed the potential for the formation of SnS_2 though as no traces were noted in tests with the Zn ternary. All these analyses tend to point to tin as the major sulfur-reactive species.

Both oxidation and sulfurization products remain on the surface as a dross upon exposure to a stack gas. Removal and concentration of the absorption products appears to be an easier process than with the molten salt systems. In addition, the thermal reduction ofsulfur-containing species in the metal system would not be affected by the presence of excess metals.

TABLE VII - TYPICAL ANALYSES FROM THE Sn-Pb-Zn ALLOY TESTS

Sample	Location	Sn (wt%)	Pb (wt%)	Zn (wt%)
Original charge		71	28.5	0.5
1	Splashed	72	27.8	0.2
2	Slurried	69	29.5	1.5)small)amount
3	Solid	68	31	1)present
4	(black) reacted	72	26.5	1.5
5	Liquid	72	28	0.1
Original charge		68	30.5	1.5
1	Splashed liquid	67.5	32.3	0.2
2	Slurried dross	63.8	36.5	0.7)large)amount
3	Solid dross	63.5	30	6.5)present
4	(black) reacted material	71	28	1
5	Liquid remaining	65	34.5	0.5

OPERATING PARAMETERS FOR METAL SYSTEMS

The difference between stirred and unstirred tests of the Sn-Pb eutectic were small. The greatest differences were observed in the efficiency and capacity for SO_2 absorption. Increasing the surface area of the contactor resulted in increasing both the rate and capacity of the bubbler, since the products form an impenetrable scum over the surface of the melt which does not readily react with the stack gas.

Tests with Sn-Pb-Zn alloy have shown that oxidation can be significantly reduced. A problem remained with the system, however, due to the separation of intermetallic phases. During tests in which the metal pool was stirred, a separate phase was formed which was high in Zn. This has been found in tests containing as little as 1 weight percent Zn, whereas it was not observed in unstirred tests containing as much as 7 weight percent Zn.

A Zn concentration of approximately 2 weight percent in the ternary alloy reduced oxidation to a minimum, even upon exposure at 450°F. Reactivity towards SO_2 was also decreased and appears to be more sensitive to the addition of inhibitors than the oxidation.

The formation of higher melting alloys and intermetallic phases during stirring and exposure to stack gases reduced the reactivity of these metals significantly. While the reaction between the gas and liquid phase removed approximately 70-80 percent of the SO_2 in these contactors, the gas went through unchanged when the viscous slurry or solid phase was formed.

A combination of decreased reactivity and gas contacting resulted in poor scrubbing efficiencies for these alloys. By increasing the residence time in the contactor, SO_2 removal was increased. In all these tests, total utilization of the metal represented only a small fraction of the reactive material.

The results of these tests show that these experimental contactors are insufficient for liquid metal systems. All previous calculations are based on a contactor similar to that used by the Imperial Smelting Company, which has been developed for industrial processes. Data obtained in the stirred contactors show a significantly increased efficiency and similar increases would be expected using the Imperial Smelter's contactor.

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APPENDIX I

PHYSICAL PROPERTIES OF MOLTEN NITRATES

The physical properties of particular interest for the engineering evaluation of inorganic fused salt systems are: density, viscosity, surface tension, heat capacity and thermal conductivity. Most of these properties have been measured for binary nitrate systems, but at higher temperatures than would be encountered in stack gas scrubbing systems.

Density

Murgulescu and Zuca (1966, 1969) have measured the density of all the binary nitrate systems in the range of 250° to 500°C. Smith et al (1964) studied binary systems including KNO_3 and Janz (1967) has reviewed and compiled all the data available through 1966. No data have been measured on ternary systems, however.

It has been established that the densities of binary molten nitrate systems are additive and can be represented by linear temperature functions. Deviations from these formulas are negligible for binary systems and densities can be safely calculated and extrapolated from data on the pure components.

The linear density equation, $\rho(g/cc) = a-bt$, has been used with reported values for the constants to calculate the densities given in Table VIII.

TABLE VIII - DENSITIES OF MOLTEN NITRATE SYSTEMS

System	Composition Mole %	$\rho = a-bt$ a	10^3b	Density at 150°C g/cc
K-Li	59-41	2.03	0.68	1.93
K-Li-Na	46-36-18	2.06	0.70	1.96
K-Na-Ca	55-16-29	2.22	0.60	2.13

Viscosity

The viscosity of molten alkali metal nitrates has been reported by Murgulescu and Zuca (1966, 1969), Janz (1967) and Protsenko (1964). Most of the data reported are for anhydrous systems at temperatures above those of normal stack gases.

Because of the uncertainities regarding the applicability of this data and the possible errors in the extrapolating the high temperature data, we measured the viscosities of several eutectic systems. Since precise measurements were not felt to be necessary, a Brookfield viscometer (Model LVF) was adapted to obtain viscosity values in the temperature range from about 140°C to 180°C.

Viscosity measurements were made on the molten eutectics contained in a 200 ml beaker. A heating mantle, surrounding the beaker regulated the temperature (± 5°F). The spindle was inserted through a heat shield to minimize overheating of the viscometer motor. Melt temperatures were measured with a chromel-alumel thermocouple immersed in the melt. The viscometer was calibrated by measuring aqueous solutions of known viscosity.

In addition to viscosity measurements the pure eutectic nitrate melts, two systems were also measured after the addition of 3 weight percent calcium oxide. The results of these measurements are given in Table IX. For comparison, the data on (K,Li) NO_3 are plotted in Figure 22 along with the higher temperature values of Murgulescu and Zuca. Reasonable agreement is obtained with the extrapolation of the relationship, $\log \eta = a + b/T$. Also shown are the values obtained for the anhydrous (K,Na,Ca)NO_3 system as compared with Protsenko's data.

The values obtained for the anhydrous (K,Na,Ca)NO_3 are significantly higher than those obtained on the hydrated melt and are more nearly in agreement with the data of Protsenko. From our experience with this system, its affinity for water is so high that even if the initial melt were anhydrous, exposure to moist flue gas would rapidly result in the melt becoming hydrated and therefore the lower range of viscosities is more valid for this system in practice.

Surface Tension

The only significant data on surface tension of nitrate mixtures are those for binary alkali metal systems reported by Bertozzi and Sternheim (1964). These measurements were made for various binary compositions from the melting points to ~ 400°C. The surface tension for each composition showed a linear temperature dependence.

Interpolation of their data on the K-Li system for the eutectic composition gives the following relationship,

$$j = 131.0 - 0.065t$$

where j is the surface tension in dynes/cm and t is the temperature

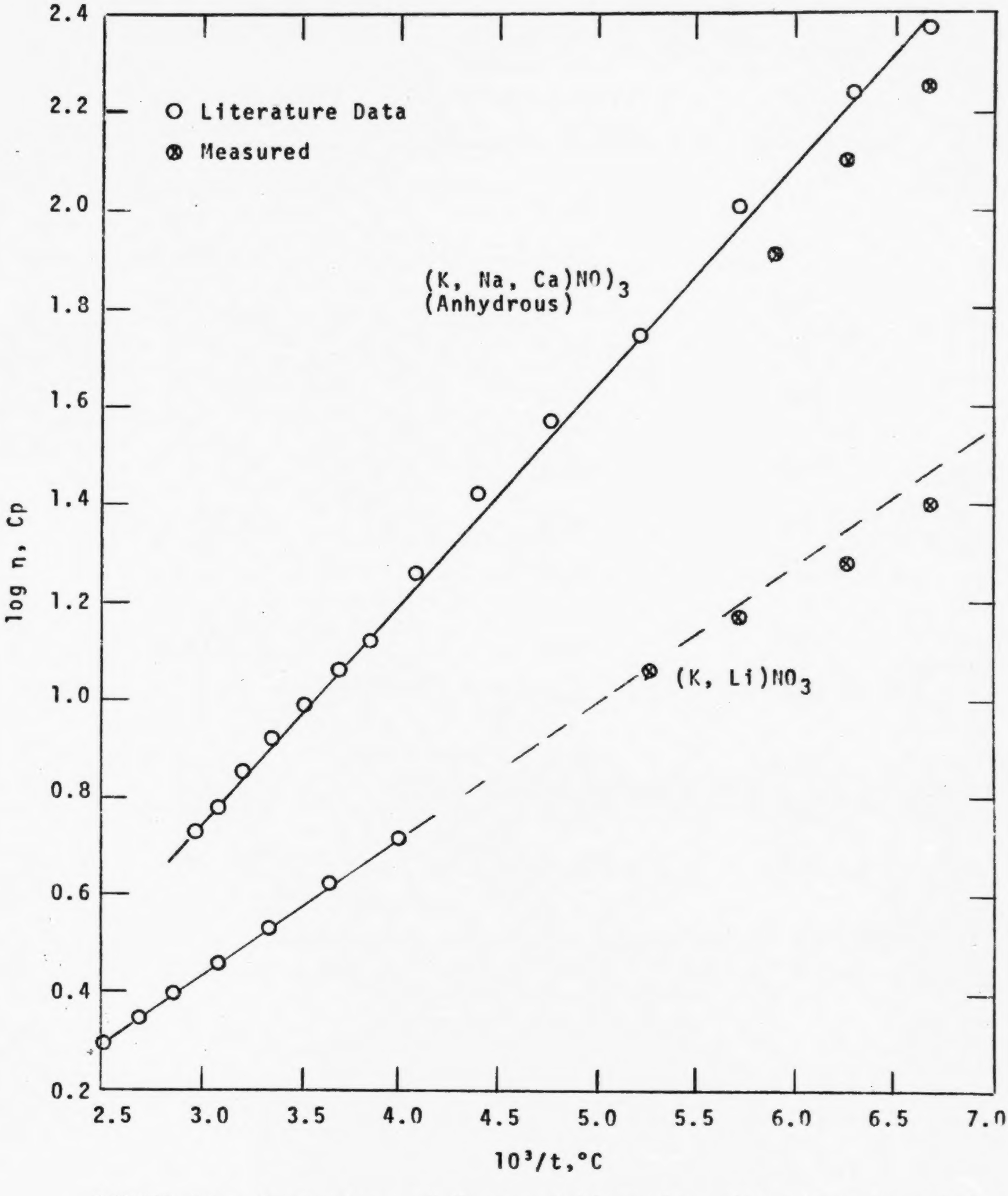

FIGURE 22 - Comparison of Measured Viscosity with Literature Data

TABLE IX - VISCOSITIES OF MOLTEN NITRATE SYSTEMS

System	Temp. °C	Viscosity, pure melt C_p	Viscosity, melt + 3% CaO C_p
K-Li	140	25.0	30.6*
	150	22.4	24.6
	160	18.6	21.2
	175	15.4	
	190	11.4	
K-Li-Na	140	23.6	
	150	18.5	
	160	15.6	
K-Na-Ca (hydrated)	150	26.0	79.4
	160	18.0	
K-Na-Ca (anhydrous)	150	180.0	
	160	127.0	
	170	81.7	

*Some settling of CaO particles during measurement.

in °C. We have estimated the surface tension of the K-Li-Na ternary eutectic from the K-Li system at 36 mole percent Li. This gives the approximate relationship,

$$j = 128.7 - 0.059t$$

for the K-Li-Na ternary eutectic.

A single value for the surface tension of $Ca(NO_3)_2$ is given by Addison and Coldrey (1961). Their results on the Group II nitrates show that the influence of cation radius is more than offset by the decrease in tension due to covalency, so that for divalent cations, the surface tension decreases with decreasing radius. As an approximation, then, we would predict the surface tension of the K-Na-Ca ternary eutectic to be similar or slightly lower than that of the alkali metal eutectics.

Thermal Conductivity

Only very limited data on the thermal conductivity of molten nitrates are available. Bloom and coworkers (1965) have reported values at several temperatures for $NaNO_3$ and KNO_3 and for mixtures of these. Based on these values and data reported by Janz (1967) on other molten salts, we estimate the thermal conductivity of all of the nitrate eutectics to be of the order of 1×10^{-3} cal/cm sec deg.

Heat Capacity

Kelley (1960) gives heat capacity values for the alkali metal nitrates. We have estimated a value for $Ca(NO_3)_2$ at its melting point. Assuming additivity, the calculated heat capacities for the nitrate eutectics are given in Table X.

TABLE X - CALCULATED HEAT CAPACITIES FOR MOLTEN NITRATE EUTECTICS

System	C_p cal/deg mole
K-Li	28.3
K-Li-Na	29.9
K-Na-Ca	39.5

Melting Points

The melting point of the (Ca-Na-K)NO_3 eutectic is reported by Clark (1968) as 133°C. Lab prepared eutectics have melted as low as 124°C, and have shown a significant dependence on the water concentration. No appreciable changes were noted with CaO present except that it was almost impossible to separate water from the oxide-nitrate mixture. This indicated the presence of hydroxide, which was later substantiated in stack gas exposure tests.

The melting point of the (Ca-Na-K)NO_3 eutectic containing 5 weight percent CaO and 0.5 weight percent $CaSO_4$ was measured as 131.5°C. Increasing the $CaSO_4$ further to 2 weight percent made negligible increases to the melting point.

Clark (1968) reports the melting point of the (K-Li)NO_3 eutectic as 133°C and that of the (K-Na-Li)NO_3 eutectic as 120°C. Both of these have been reproduced regularly in laboratory compositions and show only slight variations with oxide or carbonate additions.

Melting point of the urea-(K-Na)NO_3 eutectic is reported by Clark (1968) to be 73°C. We have reproduced this melting point, but also found that it can change with water concentration. Melting points for various lab preparations have varied between 70 and 79°C. Some of this variation may result from errors involved in the preparation of eutectic compositions as well as the water content.

Thermal stability of urea limits the operating temperatures for these systems to the range 195-230°F. No changes were noted in thermal stability of this system for any of the SO_2-reactive additives. The operation temperature range could be increased approximately 9°F by the small additions of sodium formate. A 0.5 weight percent addition of NaO_2CH was sufficient to obtain the maximum stable liquid range.

Solubility

Solubility measurements were made in 250 ml Pyrex beakers in which 60 g eutectic mixture samples were fused. The beakers were held in a heating mantle which was also used to fuse the crystalline mixtures. Aliquot samples were decanted from these melts after 30 minutes temperature equilibrium at 300°F. Hydrated water appeared to aid oxide dissolution in eutectics containing $Ca(NO_3)_2$, while it definitely deterred solubility in the ternary alkali nitrate eutectic. The precision of the data was ± 0.6 percent, indicating that homogeneous mixtures can be produced at these concentrations. The data presented in Table XI show the comparative stabilities and solubilities of the candidate fused salt systems.

TABLE XI - MELTING POINTS AND SOLUBILITIES OF CANDIDATE INORGANIC SALT SOLVENTS

Eutectic mol/o	M.P. °C	Useful (Stable) Temp. Range °C	CaO Solubility wt/o	$CaCO_3$ Solubility wt/o	$CaSO_4$ Solubility wt/o	$Ca_3(PO_4)_2$ Solubility wt/o
$LiNO_3$-$NaNO_3$-KNO_3	120	120-240	10	15	1.4	20
KNO_3-$LiNO_3$	120	120-240	10	15	3.3	20
$Ca(NO_3)_2$-$NaNO_3$-KNO_3	133	133-230	9	8	2.3	5
$CO(NH_2)_2$-KNO_3-$NaNO_3$	73	75-110	< 1	16	5.3	11

Maximum solubility of CaO in the ternary alkali nitrate eutectic was measured at 10 weight percent. The maximum solubility may be used with only a nominal increase in viscosity; which also makes it more difficult to form slurries with the oxide in this system.

The solubility of $CaSO_4$ in the ternary alkali metal nitrate was measured at 1.4 weight percent. When CaO was present at a concentration of 5 weight percent in the same melt, the solubility decreased to slightly less than 1.2 weight percent when the melt was exposed to stack gas containing 0.38 percent SO_2. Maximum solubility of $CaSO_4$ in the KNO_3-$LiNO_3$ eutectic was measured at 3.3 weight percent.

$CaCO_3$ solubility has been measured at approximately 15 weight percent in both these nitrate eutectics. The poor reactivity of $CaCO_3$ places a severe limitation on the SO_2-scrubbing efficiency of these systems, even when slurries are used. The gas-solid reaction does not help the kinetics of the absorption reaction.

Solubility characteristics of the urea-(K-Na)NO_3 eutectic are more like water than those of the ternary alkali- or calcium-alkali nitrate. Maximum solubility of $CaCO_3$ is ~ 15 weight percent in urea and 16 weight percent in the urea-(K-Na)NO_3 eutectic. Melting point data indicated a eutectic in the urea-$CaCO_3$ system containing ~ 7 weight percent $CaCO_3$. In contrast, CaO is soluble to a maximum of ~ 10 weight percent in the urea-(K-Na)NO_3 eutectic, but the mixture decomposes, releasing NH_3.

$CaSO_4$ has been found to be soluble to ~ 5 weight percent in the urea-(K-Na)NO_3 eutectic. Melting point changes in this eutectic system containing oxides, carbonates, phosphates or absorption products have been minimal.

In general, the physical and chemical properties of the nitrate eutectics used in this program are comparable to those of the patented "Hitec" eutectic. The major chemical differences stem from the nitrite content of the "Hitec" eutectic.

Kirst, Nagle and Castner (1940) measured most of the physical properties of "Hitec" and their temperature dependence. Specific gravity of the eutectic varied from 1.97 to 1.68 g/ml over the temperature range 150-558°C. The specific heat was measured at 0.373 cal/g°C and viscosity varied between 17.5 and 1.2 centipoises over this temperature range. The results of their investigation indicated that the nitrate-nitrate eutectic would be suitable for long term use to temperatures as high as 425°C.

APPENDIX II

ALTERNATIVE FUSED SALT SYSTEMS

Throughout this program, the physical and chemical properties of various inorganic liquids were investigated from both a theoretical and pragmatic viewpoint. These studies were directed towards the possible incorporation of alternative scrubbing systems into this program for evaluation.

Screening tests with fused salts have shown that candidate salt systems which are "inert" towards the stack gases have a slightly acid character. This chemical characteristic, in addition to thermal stability, appears to be the most important criterion for evaluating candidate solvents.

Early in the program the alkali acetates were chosen as candidates because of their SO_2 affinity and low melting points. They showed too great reactivity towards SO_2 even when combined with other inorganic salts. Denney (1969) has reported the solubilities of oxides and many transition metal compounds in organic salts such as sodium formate. He also lists some references for aromatic compounds and data for systems involving alkali carboxylic acid salts with nitrates.

A few rudimentary screening tests were done with alkali metal tartrates, stearates, oleates, valerates, caproates, lactates, salicylates, citrates, benzoates and phenylacetates. Contrary to some of the references cited by Denney, most of the alkali salts experienced considerable decomposition when exposed to simulated stack gas while molten.

Throughout the series of acid salts, the potassium salts gave the lowest melting points, but the sodium salts were usually the more stable. Both sodium and potassium phenylacetates have shown some thermal stability and the ability to dissolve a few SO_2-reactive oxides.

ZnO and Fe_2O_3 were used to form solutions containing more than 5 weight percent of the oxide in these solvents. Potassium phenylacetate may be used at temperatures above 120°C, while the sodium salt does not melt until 170°C. Both salts have an appreciable vapor pressure and further work will be required to determine the best method to stabilize the compounds.

One test has been completed in which sodium phenylacetate containing 5 weight percent ZnO was exposed to a simulated stack gas with 3.2% SO_2. A graph of the effluent SO_2 concentration versus time is shown in Figure 23. No attempt was made to measure the loss of the phenylacetate, but exposure to the stack gas gave no indication of increased decomposition.

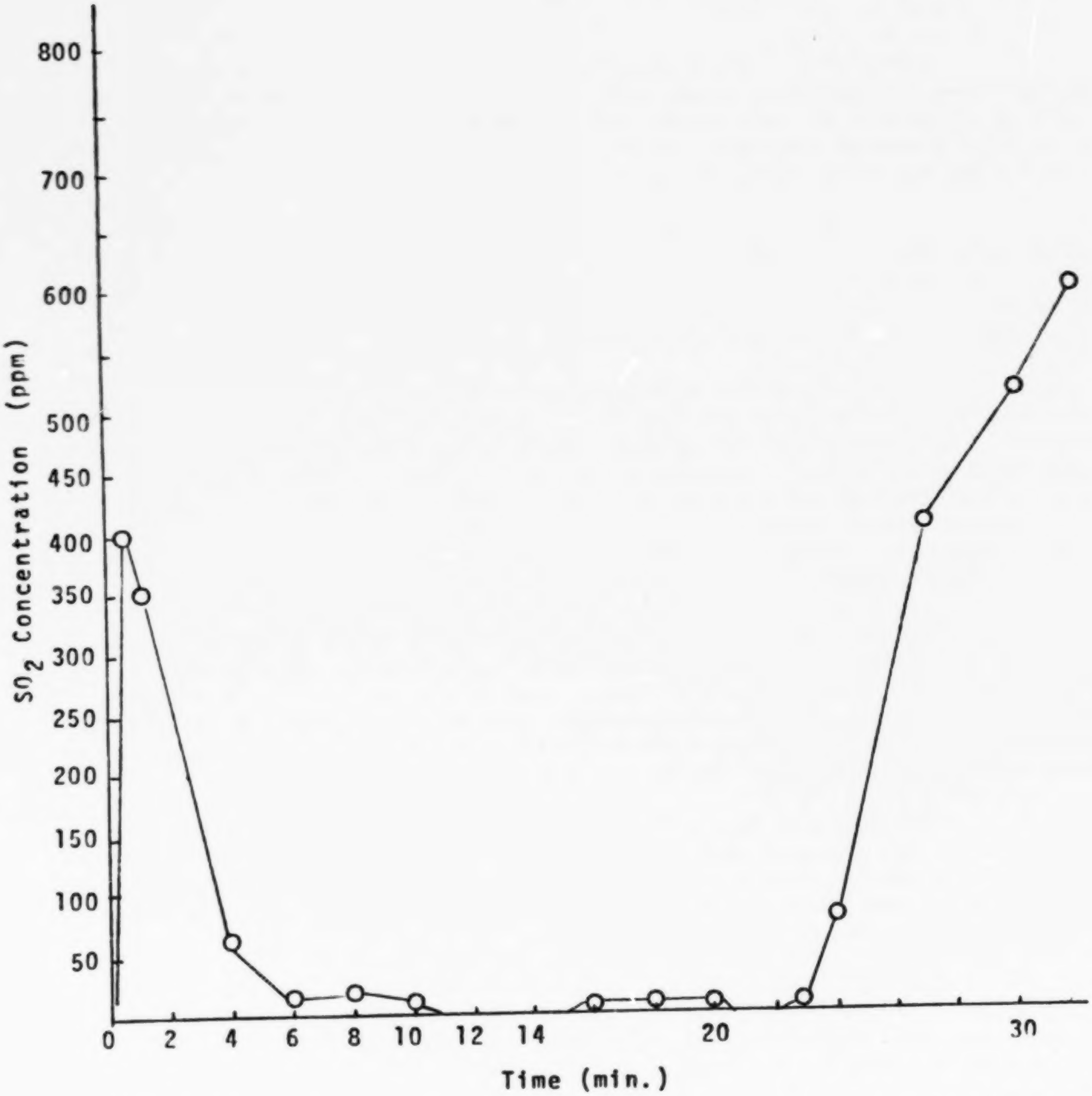

FIGURE 23 - Effluent SO_2 Concentration From a Bubbler Containing 5 wt/o ZnO in Sodium Phenylacetate (485°F) Exposed to Simululated Flue Gas Containing 1000 ppm SO_2

Some screening tests were done to see if the reaction:

$$2FeCl_3 + SO_2 + H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

could be obtained in a non-aqueous system. All attempts to dissolve $FeCl_3$ into an "inert" salt solvent have been unsuccessful. Reactivity and thermal decomposition of iron chlorides defeated attempts to utilize this reaction, or the $FeCl_2$ reaction,

$$4FeCl_2 + 4HCl + SO_2 \longrightarrow 4FeCl_3 + 2H_2O + S$$

in a fused salt system.

A chloride melt containing 46.5 weight percent $FeCl_3$-28.3 weight percent $FeCl_2$-25.1 weight percent KCl has exhibited the best thermal stability. This ternary chloride melts at approximately 200°F in the presence of water, but has been heated to approximately 300°F in a static crucible with little or no evidence of decomposition. The same melt released only trace quantities of chlorine and HCl when air was bubbled through it.

When this melt was prepared in a small bubbler and exposed to smelter gas, the removal of SO_2 from the simulated flue gas was quantitative throughout the test. The heat of reaction, however, appears to be significant and temperature excursions greater than 100°F were measured. The test was initiated at a nominal 220°F where no SO_2, H_2S, HCl or Cl_2 were discovered in the effluent gas stream. During the first temperature excursion, Cl_2 and HCl were given off. The temperature increase stopped at about 350°F, but H_2S was noted in the effluent between 325 and 350°F. As the temperature decreased, H_2S generation ceased and the effluent gas was relatively clean again. Chlorine evolution occurred soon after this with only a minute portion of the total SO_2 activity used. In addition to the reactions mentioned above, which form acids and sulfur, redox reactions forming H_2S and Fe_2O_3 took place.

The melt experienced more oxidation than anticipated from preliminary tests. The total SO_2 adsorption was so small that definitive analyses were almost impossible. Neither sulfate nor sulfur were found within the melt, which disagrees with the hypothesized reactions. A trace of iron sulfide may have been formed.

The results of preliminary tests on chloride melts indicated that systems having greater thermal stability and oxidation resistance were required. The chlorides are plagued by excess reactivity towards the constituents of stack gases. This ternary substantially increased the thermal stability of the iron chloride melts, but regulating their reactivity to the acid constituents of the stack gas appears impossible.

An attempt was also made to use dibutylphthalate as the solvent for the ferrous and ferric chlorides reactions presented in previous reports. Although the phthalate proved to be stable towards the stack gas at 300°F and ferrous chloride is soluble to approximately 10 weight percent, there was no evidence of a reaction occurring between the chloride and SO_2. The test was done in a single stage bubbler where the SO_2 concentration of the effluent gas stream equalled that in the feed gas within 45 seconds.

While screening solvents for the ferrous-ferric chloride system, sodium formate was examined as a possible solvent for inorganic salts, especially oxides. According to Denney (1969), sodium formate will dissolve considerable quantities of most of the transition metal oxides. Rough solubility measurements have been made which indicate that as much as 10 weight percent of Fe_2O_3, ZnO, Fe_3O_4 and CaO may be dissolved in the fused salt without appreciable reaction.

If the operating temperature could be increased to approximately 250°C (485°F), sodium formate could have some merit as a solvent for various substances including Na_2CO_3, Fe_2O_3 and ZnO. These compounds appear most promising as candidates for SO_2 absorption, although no tests have been done to confirm their reactivity in these systems. Both Fe_2O_3 and Fe_3O_4, although soluble, react slowly to form an oxide layer on the surface which interferes with the operation of the system. Both ZnO and Na_2CO_3 are soluble to greater than 5 weight percent, which should permit adequate reactions.

Since the reactivity of carbonates was less than the oxides in nitrate eutectics, the urea-KNO_3-$NaNO_3$ eutectic was used as a solvent for $CaCO_3$. Some data were obtained for urea-$CaCO_3$ mixtures which show that the melting point decreased until the $CaCO_3$ concentration exceeded approximately 10 weight percent. Concurrently, the addition of $CaCO_3$ lowered the decomposition temperature of the mixture slightly ($\sim$3°C).

When the urea-$CaCO_3$ mixture was exposed to a simulated stack gas concentration, no SO_2 was found in the effluent gas stream. The melting point of the mixture increased until decomposition of the urea gave a significant NH_3 concentration to the effluent. After opening the bubbler it was found that the decomposition of urea had not only followed the usual pattern for the production of NH_3, but that a measurable concentration of nitrate was formed as well. No effort was made to define the mechanisms or extent of these undesirable reactions.

By utilizing the urea-KNO_3-$NaNO_3$ eutectic, the operating temperature was lowered significantly. Although the eutectic melts at 75°C, the addition of $CaCO_3$ to a concentration of 4.5 weight percent raised the melting point and the system was operated at approximately 105°C.

SO_2 was again absent in the effluent from the bubbler. Both carbonates and sulfates seem to have greater solubility and are more easily suspended in the urea-nitrate eutectics than in nitrates alone. The sulfates formed by the absorption of SO_2 were found uniformly throughout the melt, confirming these solubilities.

Binary and ternary eutectics containing alkali and alkaline earth hydroxides were also studied. These eutectics all melt at the highest temperatures (220-250°C) which would be available in stack gas scrubbing installations. Their reactivity towards CO_2 in the atmosphere limits their applications for these systems, but alkali nitrate-hydroxide eutectics showed some promise during screening tests.

KNO_3-KOH and KNO_3-$NaNO_3$-NaOH eutectics were thermally stable and would dissolve some of the transition metal oxides as possible SO_2 absorbers. These were the only systems of this type which showed sufficient stability and the capability of reacting with SO_2 in a stack gas to form workable mixtures.

Carbonate was the major product of exposure of the nitrate-hydroxide melts to air or stack gas mixtures. This absorption caused a deterioration of the hydroxide eutectic with a commensurate increase in melting point, and usually resulted in the precipitation of carbonate. Since the concentration of CO_2 in the simulated stack gases far exceeds that of SO_2, the formation of carbonate is the main reaction occurring within the melt.

The limited reactivity of the carbonate formed in hydroxide and nitrate melts reduced the efficiency of these melts. The formation of a solid carbonate phase also eliminates the advantages obtained from a liquid system. The limited reactivity and kinetics of gas-solid reactions make these mixtures unpromising as inorganic liquid stack gas scrubbers.

Phosphate Systems

Evolving out of the studies of adduct-forming scrubbers, the examination of phosphate systems has been undertaken as an expansion on the apparent ability of these fused systems to oxidize SO_2 to SO_3. Several phosphates have been dissolved in the eutectic nitrate solvents and found compatible with stack gases. Dissolution of the phosphates initially lowered the

the melting point of the nitrate solvent. As the phosphate concentration increased, both the melting point and viscosity of the mixture increased.

Calcium phosphate was the first of this group to show desirable characteristics upon exposure to simulated stack gas. Initial screening tests showed minimal absorption of SO_2, but indicated the presence of other reactions which could also be incorporated in a stack gas scrubbing scheme.

Maximum solubility of $Ca_3(PO_4)_2$ in the $(K\text{-}Na\text{-}Li)NO_3$ eutectic appears to be approximately 20 weight percent. At this concentration, the melting point has been raised to 130°C and the viscosity increases to nearly twice that of the pure nitrate eutectic. Solubility in other nitrate eutectics is less, being approximately 5 weight percent in the $(Ca\text{-}Na\text{-}K)NO_3$ eutectic, and the influence on viscosity is more pronounced. Much of the interference involved in all these systems regarding both solubility and viscosity appeared to depend upon the hydrated and absorbed water held in the system. Exposure to a simulated stack gas containing 10% water did not permit operating with anhydrous fused salts.

When these mixtures were used in a bubbler contactor to scrub a simulated stack gas, SO_2 was absorbed initially for a few minutes. The concentration of sulfur oxides in the effluent stream increased rapidly after this brief absorption. The SO_x concentration in the effluent gas streams approaches that in the simulated stack gas as the exposure time increases.

Effluent SO_2 concentration was greater than the concentration of the stack gas delivered, when an SO_2-LIRA was used to monitor the effluent gas stream. Several alternative analytical methods (described previously) were used to analyze the effluent. The results of these "on-stream" measurements did not agree with mass spectrometer analyses of the simulated stack gases.

Although these different analyses have shown general agreement, there is some overlap. The blanks found necessary for correlating the results of these "in-stream" measurements do not agree with the mass-spectrometer analyses of the simulated stack gases. These discrepancies are reflected in the reported data.

After comparing the results of analyses using wet chemical, infra-red and vapor-phase reactions, it appears that a portion of the SO_2 concentration occurring in the stack gas is oxidized to SO_3. An explanation of these reactions has been published by Hughes and Cameron (1931). Although a complete definition of the reaction mechanisms and products formed exceeds the scope of this problem, some analyses have been performed to investigate the feasibility of these systems as inorganic liquid stack gas scrubbers.

Several phenomena were observed during these tests which confirm the formation of SO_3: (1) the standard technique of isopropanol-water and iodine bubblers has measured high concentrations of SO_3, but it has had very high blank determinations also; (2) when $Ca_3(PO_4)_2$ and CaO were dissolved simultaneously in the (K-Na-Li)NO_3 eutectic and exposed to a simulated stack gas, the predominant product was sulfite and some NO_x was detected in the effluent gas; (3) a bubbler containing $Ca_3(PO_4)_2$ in the nitrate eutectic was placed in the gas stream before the usual CaO bubbler, resulting almost exclusively in the formation of sulfate and releasing considerable amounts of NO_x in the effluent.

Several investigations have been made into the kinetics and mechanisms of reactions by which SO_2 is oxidized. Oxidation by manganese sulfate aerosols has been examined by Matteson, Stöber and Luther (1969). Bassett and Parker (1951) dealt with the general area of oxidation and found that manganese salts, particularly $MnSO_4$, were the most efficient. From the very first work of Johnstone and Coughanow (1958), however, the reaction has been postulated as proceeding through an SO_2 adduct.

An explanation of these reactions may be made on the basis of the formation of $CaHPO_4$ and $Ca(H_2PO_4)_2$, as reported by Hughes and Cameron (1931); by the formation of $Ca(PO_3)_2$; or by the formation of adducts or complexes which are unstable at the operating temperature. Although the complete identification of compounds and mechanisms is beyond the scope of this program, it is necessary to perform some crude tests to identify the products and estimate the feasibility of such a system in proposed stack gas scrubbing facilities.

We have followed the qualitative separation scheme of Hughes and Cameron (1931), separating the products by solubilities. Approximately one-half (by weight) of the original $Ca_3(PO_4)_2$ charge was soluble in an ammonium citrate solution. This represents the fraction of $CaHPO_4$, according to Hughes and Cameron. Approximately three-tenths (by weight) of the original $Ca_3(H_2PO_4)_2$ charge was soluble in distilled water. This represents the $Ca(H_2PO_4)_2$ fraction. There was no evidence of solubility changes occurring in the nitrate melts, a phenomenon which would optimize the use of phosphates for SO_2 scrubbing.

Overall oxidation of SO_2 entering these phosphate bubblers has been in the order of 20%. After the initial absorption, oxidation increases from approximately 0.1% to 20% within tens of minutes. One exception was found using the ternary nitrate eutectic containing 25 weight percent $Ca_3(PO_4)_2$. In this case, absorption continued for nearly 40 minutes during which time only about 25% of the total SO_2 input was measured in the effluent stream. Even in this unique case, however, the SO_3 concentration increased slowly as sulfur values increased in the effluent.

Data from this test mixture containing 25 weight percent $Ca_3(PO_4)_2$ are presented in Table XII. As indicated, no SO_x was detected in the effluent gas during the first five minutes.

TABLE XII - SO_2 OXIDATION

Exposure Time, Min.	SO_2 Concentration of Input, ppm	Effluent Gas Stream SO_2 Conc. ppm	Effluent Gas Stream SO_3 Conc. ppm
0	32,000	0	0
5	32,000	0	0
10	32,000	6,200	400
25	32,000	6,300	600
40	32,000	6,700	1,100

Although only a fraction of the total sulfur concentration continued through the bubbler, the SO_3 concentration increased at a similar proportional rate. If the reactions mentioned previously by Hughes and Cameron (1931) were mass action dependent (as most such reactions) these phenomena would be anticipated.

Similar tests with mixtures containing lower concentrations of $Ca_3(PO_4)$ had little or no concentration of SO_2 in the effluent gas stream. As indicated above, this should be the result of more efficient contact with a less viscous fused salt and the lesser probability of continued reaction with the phosphate. The reaction sequence appears to be one in which a short induction time is necessary during which absorption, oxidation and rearrangement to form acid (hydrogen) salts and, eventually, the sulfate. The steps appear to follow according to:

Ia. $Ca_3(PO_4)_2 + SO_2 \longrightarrow Ca_3(PO_4)_2 \cdot SO_2$

Ib. $Ca_3(PO_4)_2 + SO_2 + 1/2\ O_2 \longrightarrow Ca_3(PO_4)_2 \cdot SO_3$

Lundquist (1963) reports such adducts for several compounds including $MgSO_4$; $NiCl_2$; $BaCrO_4$; $MgSO_3$ and $MnSO_4$.

II. $Ca_3(PO_4)_2 \cdot SO_x + H_2O \longrightarrow CaHPO_4 + CaSO_4$

III. $Ca_3(PO_4)_2 \cdot SO_x + H_2O \longrightarrow Ca(H_2PO_4)_2 + CaSO_4$

As further support for this type of reaction, we have followed the qualitative separation of products by solubilities. Averaging the results obtained on several tests with different concentrations of $Ca_3(PO_4)$ dissolved in the ternary nitrate eutectic, 25% of the original $Ca_3(PO_4)_2$ charged has been found to be soluble in distilled water. This fraction of material corresponds to reactions such as Number III listed above.

An additional 50% of the original $Ca_3(PO_4)_2$ charged was found to be soluble in a citrate solution. This would confirm the existence of reactions such as that listed in Number II above. The remainder of the $Ca_3(PO_4)_2$ charge could be ascribed to the last acid-soluble portion of the solubility tests. Further analyses for phosphate and sulfate would be necessary, however, to take full advantage of this system in a stack gas scrubbing system.

Further data requirements for this system include:

1. Solubility of the $HPO_4^{=}$ and $H_2PO_4^{-}$ components.
2. Evaluation of the possibilities for using phosphate minerals or mixed phosphate rock as reactant.
3. The quality and performance of water-soluble phosphates from this type of process.
4. An investigation into the amounts, nature and costs of losses in such an operating system.

The primary intended purpose of these phosphate bubblers would not be as single stage SO_2 absorbers, but rather involve several stages with the production of salable products either through further reaction with more phosphate or subsequent removal reactions with the SO_3 produced.

The data generated in these tests indicate that, although the phosphates will not absorb SO_2 to the extent or with the efficiencies of the CaO mixtures, they could be used as an initial stage in the oxidation of SO_2 to SO_3 for the intended purpose of forming a more reactive sulfur compound. Several investigations are presently under contract to devise catalysts which would oxidize the SO_2 content at 95-100% efficiency for removal as H_2SO_4. These systems would not supplant the catalytic processes, since their efficiency is far below the desired level, but they do offer an alternative route for low temperature oxidations.

After the use of $Ca_3(PO_4)_2$ in nitrate eutectics had been established, other phosphates were tested to determine if these mixtures could be formed and possibly extend the field into more reactive mixtures. $FePO_4$, $Zn_3(PO_4)_2$ and $Ba_3(PO_4)_2$ have been used in similar tests as alternatives for the initial calcium compound. The relative order of SO_2 oxidation is shown in Table XIII.

These compounds were chosen as candidate materials on the basis of calculated reactivities, solubilities and thermal stabilities of the phosphates and sulfur-containing products which might occur.

Screening tests for $FePO_4$ and $Zn_3(PO_4)_2$ were developed to determine if these compounds reacted similarly to $Ca_3(PO_4)_2$ and if the sulfur-containing products could be selected for desirable regeneration characteristics.

After these initial tests with $Ca_3(PO_4)_2$ as an oxidizing additive to the nitrate eutectics, the investigation was expanded to include phosphates of iron, barium, magnesium and zinc. Screening tests for the phosphates were developed according to the needs for (1) low cost, (2) least stable absorption products, to aid absorption. In addition, $BaCrO_4$ was tested again according to the analytical scheme developed for phosphates and found to have similar reactions.

$FePO_4$ was found to be much less soluble in the nitrate eutectics than any of the other candidates. It did not show any tendency to oxidize SO_2 to SO_3 as with the calcium salt. When simulated stack gases were passed through bubblers containing $FePO_4$ mixtures there was no change in the SO_2 concentration. Analysis of the fused salt melt also failed to establish the formation of any sulfate. Fe compounds have been reported by Pechkovskii and Mal'tseva (1965) to be less reactive towards SO_2.

Tests with $Zn_3(PO_4)_2$ in the urea-(Na-K) nitrate eutectic have shown that it performs similar to the calcium salt.

TABLE XIII

ORDER OF OXIDATION EFFICIENCY IN FUSED SALTS

1. $Ca_3(PO_4)_2$ in $(K\text{-}Na\text{-}Li)NO_3$ Eutectic
2. $MnSO_4$ in $(K\text{-}Na\text{-}Li)NO_3$ Eutectic
3. $Zn_3(PO_4)_2$ in Urea $(K\text{-}Na)NO_3$ Eutectic
4. $BaCrO_4$ in $(K\text{-}Na\text{-}Li)NO_3$ Eutectic
5. $Mg_3(PO_4)_2$ in $(K\text{-}Na\text{-}Li)NO_3$ Eutectic
6. $MnSO_4$ in Urea-$(K\text{-}Na)NO_3$ Eutectic
7. $Ba_3(PO_4)_2$ in $(K\text{-}Na\text{-}Li)NO_3$ Eutectic
8. $FeHPO_4$ in Urea $(K\text{-}Na)NO_3$ Eutectic
9. $Mn_3(PO_4)_2$ in Urea $(K\text{-}Na)NO_3$ Eutectic
10. $Mg_3(PO_4)_2$ in Urea $(K\text{-}Na)NO_3$ Eutectic

Approximately 70% of the SO_2 entering the bubbler was released as SO_3 while about 25% is retained within the melt.

Tests using $Zn_3(PO_4)$ in the ternary alkali nitrate eutectic have shown that it displays the same reactions noted in the $Ca_3(PO_4)_2$ mixtures. Approximately 70% of the SO_x concentration passed through the melt and is accountable as SO_3 while only approximately 25% is retained as sulfate.

Both $Ba_3(PO_4)_2$ and $BaCrO_4$ were chosen as candidates for these tests because of the similarity to $Ca_3(PO_4)_2$. Most minerals containing Ca have Ba impurities which should react similarly. $BaCrO_4$ was tested in Phase I of this program as a candidate to scrub SO_2 by adduct formation. Although it had a good solubility ($\approx$20 weight percent), it was found to exhibit poor absorption. Since no attempts were made to identify SO_3 in the effluent of these initial screening tests, further tests in this Phase II study were deemed necessary.

Several attempts were made to realize the reactions of the iron chlorides with SO_2. Wardlow et al (1920) have reported the reactions; i.e.:

$$2FeCl_3 + SO_2 + H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2\ HCl$$

$$4FeCl_2 + 4HCl + SO_2 \longrightarrow 4FeCl_3 + 2H_2O + S$$

to occur in aqueous media. Mixtures of fused chlorides, nitrates, mixed nitrate-nitrites and urea-nitrate mixtures were used as possible solvents or carriers for these compounds.

None of these tests were successful at realizing the above reactions. Some absorption was found to occur in almost all tests, but the products were seldom desirable and usually chlorine was liberated. $FeSO_4$ and FeS_x were the most common products, although there was little or no reaction of the iron compounds in some tests.

Reactions of the chloride solvents have been noted previously. In all tests where halogens were present, a trace concentration of free halogen or hydrogen halide was released. This tendency of the halides was augmented by the thermal instability of Fe^{II} and Fe^{III} chlorides. The presence of water vapor in the stack gas also contributed towards the instability of these systems. A series of tests in which the $FeCl_3$ concentration was reduced stepwise from 8 weight percent to 1 weight percent in the urea-KNO_3-$NaNO_3$ eutectic pointed up the fact that halogen evolution was nearly independent of the halide concentration. A typical test in this series released a measurable amount of Cl_2 after only 3 minutes of exposure to a simulated flue gas.

Several different solvents were used in attempts to use the iron chlorides-SO_2 reaction in stack gas scrubbers. The chemical reactivity of the iron chlorides has precluded their use in all systems investigated. The formation of H_2SCl_2 and/or HCl has interfered with the desired reactions to an extent where the gas is polluted at concentrations equal to or greater than the original mixture. At the present time, it does not appear feasible to use the $FeCl_2$-$FeCl_3$ reactions with SO_2 under the conditions occurring in a stack gas.

All of these tests have been unsuccessful when attempting to use high temperature, molten-salt media. It appears useless to try to incorporate these reactions in this type of system.

Absorption by Two Bubblers in Series

When the effluent gas stream from a phosphate bubbler was directed into a CaO bubbler, no S-containing compounds were found in the effluent from the CaO bubbler. Sulfite was the major product in the CaO bubbler, even though the flow rate was low. Nitrogen oxides were detected in the effluent at a concentration of about 10 ppm after the amount of SO_2 delivered to the absorbers was equal to one-third the concentration of the oxide.

Calcium sulfate was again the major sulfur-bearing constituent, but an appreciable portion of the sulfur was found as sulfite. Analysis of the nitrate melt after exposure to fly ash (without CaO present) revealed that better than 90% of the sulfur contained in the fly ash (approximately 3% S) was removed. This was found as soluble sulfates, sulfites and some $CaSO_4$. Analysis of a similar melt used in a bubbler test showed only a trace of water-soluble (alkali metal) sulfates.

Apparently the oxidation of SO_2 to SO_3 impairs the use of nitrate solvents by increasing its acidity to the point at which the reaction with the weakly acidic nitrate may proceed even in the presence of oxide.

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APPENDIX III

CONTAINMENT METAL CORROSION FROM CANDIDATE FUSED SALTS

Corrosion by fused salts has received considerably more investigation with their increased use in industrial processes as fluid fuels and heat-exchanger fluids. Data generated from such investigations have been compiled by MacKenzie (1959), Bettis et al (1957), and Kirst et al (1940).

Most of the data have been obtained on pure salts or eutectic compositions. The extensive use of "Hitec," duPont's salt mixture, as a heat-treating medium provides the most complete and comparable corrosion data. This nitrite-nitrate mixture was mentioned previously as a candidate solvent in this program because of its similarity to the nitrate eutectics.

Modern metallurgical developments have practically eliminated problems of fused salt corrosion. Only a few possible exceptions are extant, such as nuclear energy installations, where ultimate passivity is necessary to prevent contamination of the process stream.

Circumventing corrosion problems by using modern exotic alloys is an expensive alternative, however. Since SO_2-scrubbing systems are being developed primarily for utilities, this added expense would nullify many SO_2 absorption attributes. Nitrates are only mildly corrosive and the object of these tests was to select those materials which could be used for a permanent economical installation.

Background

The nitrate-nitrite mixture known as "Hitec" was tested early in this program as a possible solvent for SO_2-reactive species. This mixture has been known and used for years in heat-treating metals. It has also received considerable investigation regarding physical and chemical properties since it has been used as a heat transfer medium.

The similarity of this mixture, approximately 40 weight percent $NaNO_2$ - 7 weight percent $NaNO_3$ - 53 weight percent KNO_3, with the nitrate eutectics permits a considerable amount of correlation in the physical and chemical properties between the two fused salts.

For most applications, solubility and oxidation are the primary modes of corrosion in fused salts. Solubility of metals in fused salts is usually limited to their own salts. Halides are the most aggressive molten salts, since metal-salt solubility is greatest for this class.

Since most fused salts are ionic, electrochemical reactions are an important aspect of all corrosion. Redox reactions are important criteria for evaluating possible corrosion within a fused salt system. The basic essentials for making a system immune to corrosion are: 1) the choice of container materials which will not take part in replacement or insertion reactions; and 2) removal of any reducible ions or impurities from the system. The rate of corrosion occurring in systems where these two factors cannot be selected will be controlled either by diffusion and mass transfer or the geometry of the system.

In a molten salt or metal system such as those proposed in this program, neither diffusion or contact area can be used to control corrosion. The corrosion potential in such a dynamic system is maintained at its peak level by the continuous renewal of fresh material and the volume of gas to be scrubbed necessitates large equipment.

Temperature gradients within these systems will also set up thermal potentials which promote mass transfer. Mass transfer in fused salts is essentially electrolytic, requiring an electrical path from hot to cold zones. Both the ionic salt and metal container can supply this path. For alloys, the corrosive attack usually occurs as the result of selective reactivity with one or more of the alloy constituents.

Absorption of oxidizing species such as O_2 and H_2O from the atmosphere is another parameter of fused salt corrosion. Insertion of impurities such as these into an otherwise stable fused salt system increases the redox potential, aiding oxidation "corrosion" of the metals.

It is convenient that the fused salts which are stable (inert) towards the stack gas mixtures are also the least corrosive towards containment materials. The nitrate eutectics studied in this program are both physically and chemically similar to the patented eutectic salt, "Hitec," which is commercially available from duPont.

Experimental

Armco iron and mild steel were chosen as the test materials for corrosion tests. The iron was more than 99% pure and was chosen to represent the class of pure metals, having no corrosion inhibitors, being susceptible to oxidation and possible reaction with the nitrates.

Mild steel has been reported by Kirst et al (1940), MacKenzie (1959) and Janz and Reeves (1967) to be a good containment material for pure nitrates. This was chosen as a comparison for the pure metal and representing a convenient and economical fabricating material.

Samples of Armco iron were prepared from 0.005 inch thick foil. Each sample was one-half inch wide and three inches long. Mild steel samples were cut from 0.160 inch sheet to the same dimensions. The samples were positioned in the apparatus so as to have approximately one half within the fused salt.

Several samples of these metals were exposed to a fused salt melt for 210 hours. The test was carried out in two phases which were designed to show the differences between pure fused nitrate and the oxide-sulfate containing fused nitrate occurring in a stack gas scrubbing system.

Two samples of each material were placed in the fused salt bath in the apparatus shown schematically in Figure 24. Large temperature fluctuations were experienced during the first 78 hours of exposure. The average temperature during this period was 140 ± 10°C. Temperature fluctuations in the hood area, where this apparatus was located, and problems with the electrical controls were corrected for the latter part of the test. Temperature during the last 162 hours of exposure was 146 ± 5°C.

Following this initial exposure to the (K-Na-Li)NO_3 eutectic, one sample was removed and prepared for analysis. The other sample was retained and a new sample tab of each material was added to the melt.

Temperature fluctuations during this test were smaller. The average temperature was 151°C with excursions of ± 5°C. The stirrer was used only during the regular work day, as in the preceding part of the test.

Results

Corrosion of these representative metals was minimal in the fused nitrate eutectic. As seen in Figure 25, fused nitrate attack of Armco iron is minimal within the melt for as much as 420 hours of exposure. The only attack noted was at the fused salt-air interface. Weight losses were negligible on an analytical balance.

Oxygen and water vapor in the air were mentioned previously as documented factors in fused salt corrosion. As shown in Figures 25 and 26, attack and dissolution occurred over a small area at the interface, with little or no change to the matrix material.

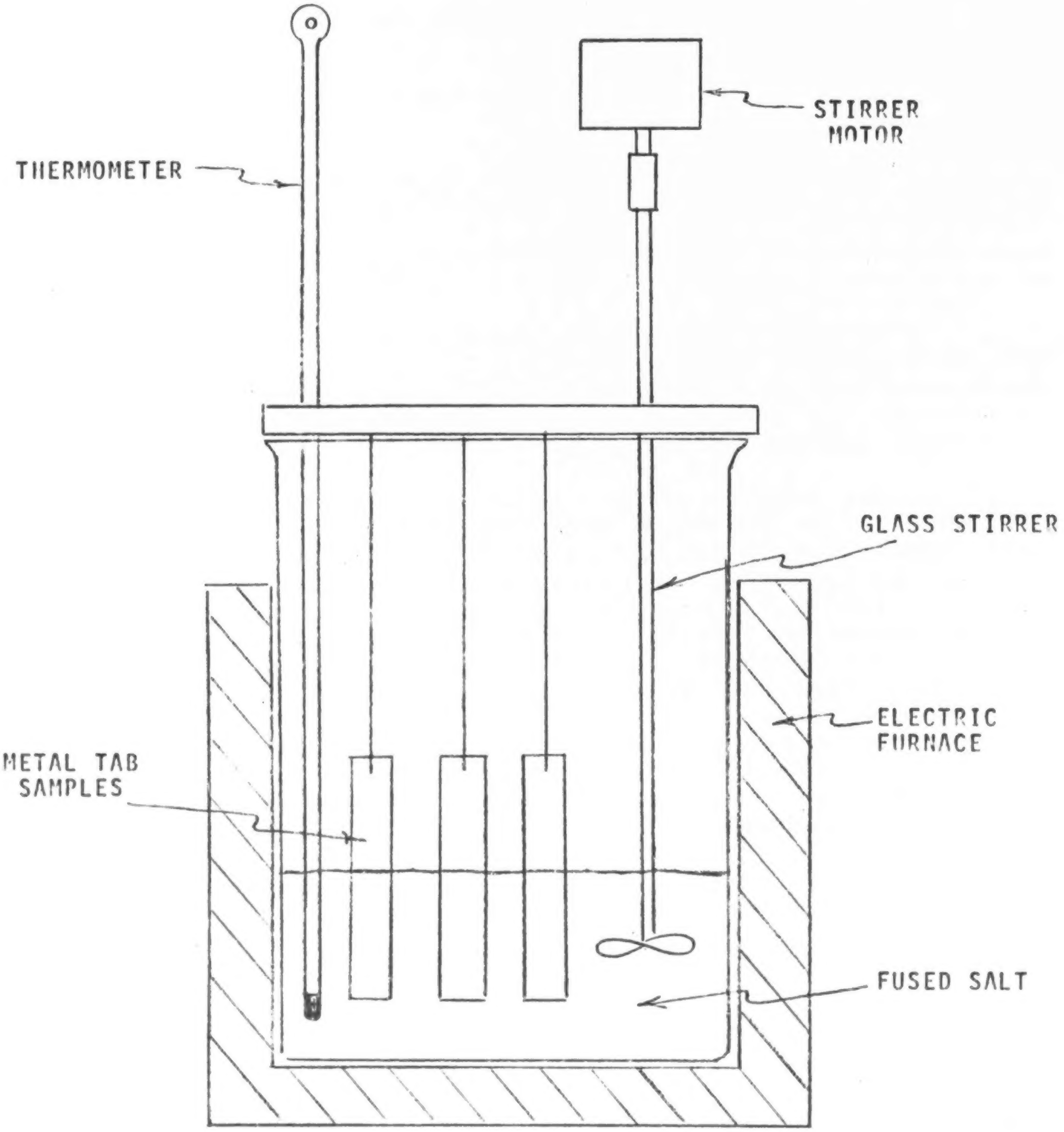
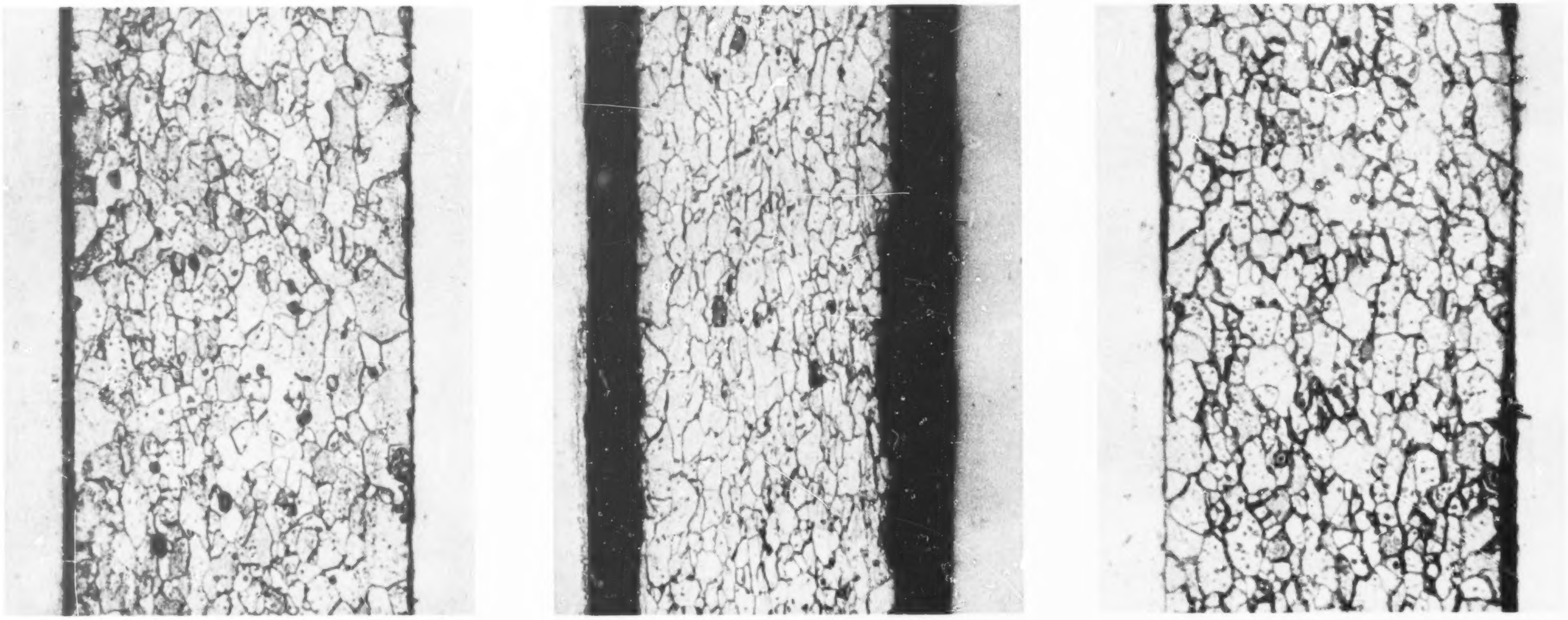

STIRRER MOTOR
THERMOMETER
GLASS STIRRER
ELECTRIC FURNACE
METAL TAB SAMPLES
FUSED SALT

FIGURE 24 - Fused Salt Corrosion Apparatus



a) 400X Tab exposed 210 hours to pure nitrate eutectic

b) 400X Tab exposed 210 hours to pure nitrate eutectic and 210 hours to nitrate eutectic containing 3 Wt% CaO

c) 400X Tab exposed 210 hours to nitrate eutectic containing 3 Wt% CaO

FIG. 25 - ARMCO IRON SAMPLE EXPOSED TO MOLTEN (K-Na-Li)NO_3 EUTECTIC

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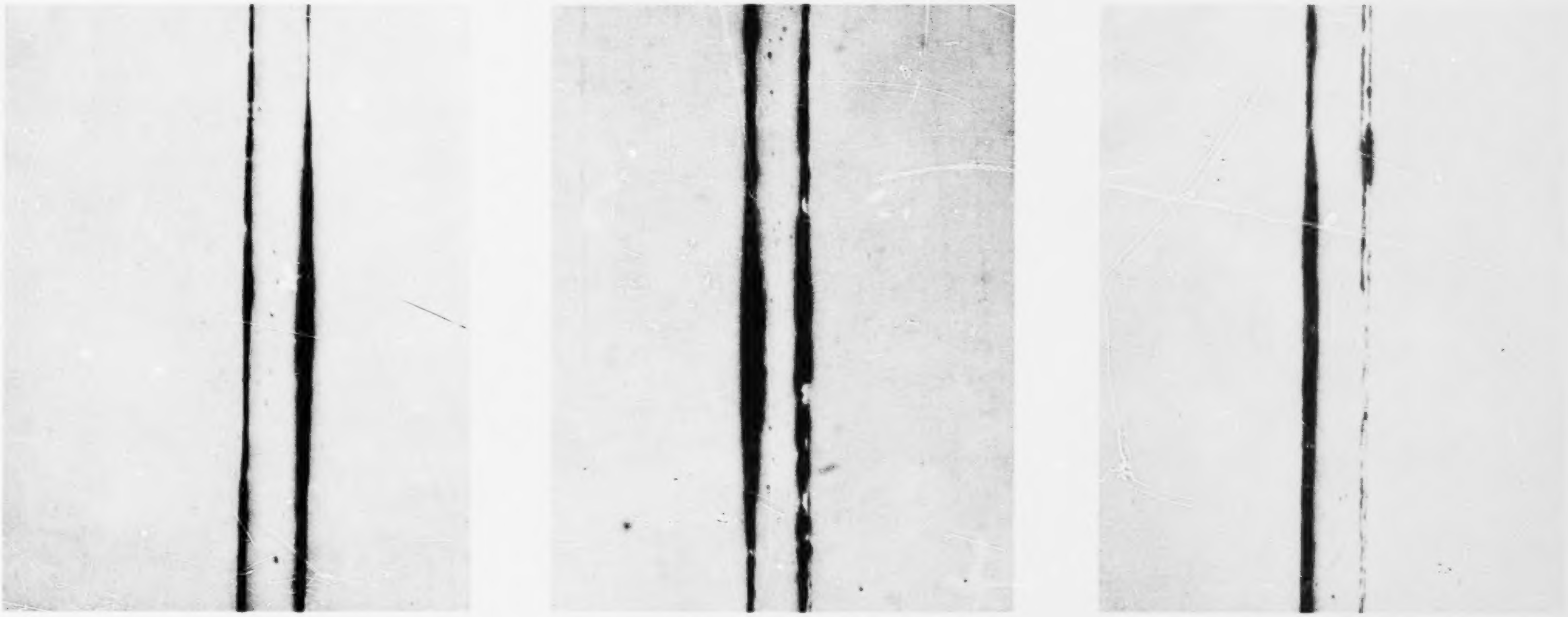

a) 66X Tab exposed 210 hours to pure nitrate eutectic

b) 66X Tab exposed 210 hours to pure nitrate eutectic and 210 hours to nitrate eutectic containing 3 Wt% CaO

c) 66X Tab exposed 210 hours to nitrate eutectic containing 3 Wt% CaO

FIG. 26 - ARMCO IRON SAMPLE EXPOSED TO MOLTEN (K-Na-Li)NO_3 EUTECTIC (as polished)

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Approximately 2.5 mil was removed from both sides of the sample during the 210 hours of exposure time. This corresponds to a corrosive attack of 104 mil/year, which is fairly severe for equipment of this type. It should be noted that there was no difference noted in the attack on the specimen exposed to the nitrate eutectic containing CaO.

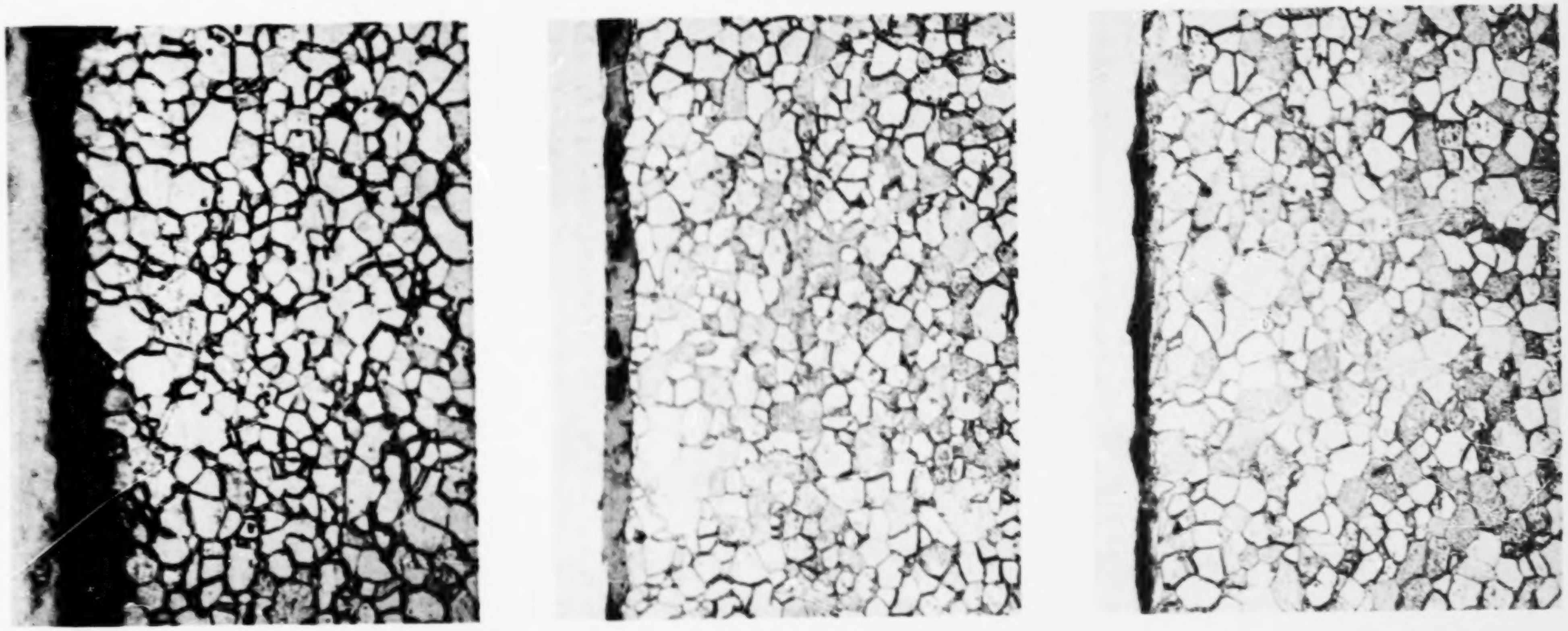
The sample exposed to both pure eutectic salt and the eutectic containing 5 weight percent CaO experienced an attack of 5.0 mil at the interface surfaces. The rate of attack was constant at 0.012 mil/hr through 420 hours of exposure.

Corrosive attack on mild steel samples was almost negligible. Both pure nitrate salt and the fused salt containing 5 weight percent CaO made negligible changes in the appearance of the mild steel samples. No weight losses were measured and no dimensional changes were observed, even under microscopic examination.

A slight amount of recrystallization is evident in Figure 27. This can all be attributed to thermal effects from exposure rather than the salt.

As with physical properties, comparisons can be made regarding the relative corrosivity of "Hitec" and the nitrate melts. Kirst, Nagle and Castner (1940) report that open-hearth steel exhibits satisfactory corrosion resistance below 850°F. Corrosion tests with this steel gave a rate of 0.3 mil penetration per month of exposure at 850°F. Copper was corroded at a rate of 30 mil per month under similar conditions.

Data obtained from these tests agree with the results of Kirst et al (1940), Bettis et al (1957) and MacKenzie (1959). Mild steel appears to be a suitable fabricating material for all equipment which will have a maximum temperature exposure of 500°F. This would include all portions of the absorption unit and recycling equipment. Higher temperatures and the evolution of SO_2-SO_3 mixtures in the regeneration step would necessitate using more exotic alloys for the regenerator. High alloy stainless steels will probably suffice for this unit, which would require a much smaller apparatus in the proposed carbo-thermic reduction scheme. Proper design of the regeneration equipment may allow the use of conventional metals lined with ceramic brick. Such practice is commonplace in analagous metallurgical operations.



a) 533X Tab exposed 210 hours to pure nitrate eutectic

b) 533X Tab exposed 210 hours to pure nitrate eutectic
and
210 hours to nitrate eutectic containing 3 Wt% CaO

c) 533X Tab exposed 210 hours to nitrate eutectic containing 3 Wt% CaO

FIG. 27 - MILD STEEL SAMPLE EXPOSED TO MOLTEN (K-Na-Li)NO_3 EUTECTIC

APPENDIX IV

EXPERIMENTAL DESIGN CALCULATIONS

In the early stages of the experimental program, some calculations were made in order to design experimental apparatus which would allow simulation of real scrubber conditions. Although such scrubber simulation was not carried out, primarily as a result of conference discussions with the Project Officer, these calculations are included in the section below.

Initial studies were directed toward the design of laboratory experiments that would be meaningful in terms of engineering evaluation. Consideration of flue gas flow in typical power plant installations shows that, in order to simulate these flow conditions in laboratory experiments, large volumes of flue gas must be used to obtain reasonably similar gas velocities; i.e., in the range of from two to as high as thirty feet per second. This is shown in Figure 28 in which U, the gas velocity, is given as a function of log G, the volumetric flow rate, for various diameter ducts. Lines of approximately constant Reynold's number, R_e, are also shown in order to illustrate the regions of laminar or turbulent flow.

From these calculations, it is seen that, regardless of the design of the SO_2 scrubber, volumetric flow rates of the order of a few hundred to over a thousand cubic feet per hour are necessary for even quite small equipment. In order to run experiments for reasonable lengths of time, these volumes of flue gas become quite difficult and expensive to obtain from cylinder storage. Preliminary investigation of the feasibility of producing such volumes of flue gas from combustion of available fuels led to the conclusion that the most simple and economical method of producing flue gas would be from the combustion of natural gas.

The most important constituent of the flue gas stream, aside from the SO_2, is oxygen, because of its influence on the chemistry of the SO_2 reactions. As shown in Table XIV, the oxygen content of the flue gas from natural gas combustion can be adjusted to match that from coal combustion by maintaining the excess combustion air at about 20 to 25 percent. This amount of excess air gives complete gas combustion under normal gas burner operation.

The appropriate amount of SO_2 would then be injected from cylinder storage into the hot flue gas. Later, NO_x and possibly flyash, could be metered into the flue to more closely simulate coal-fired flue gas.

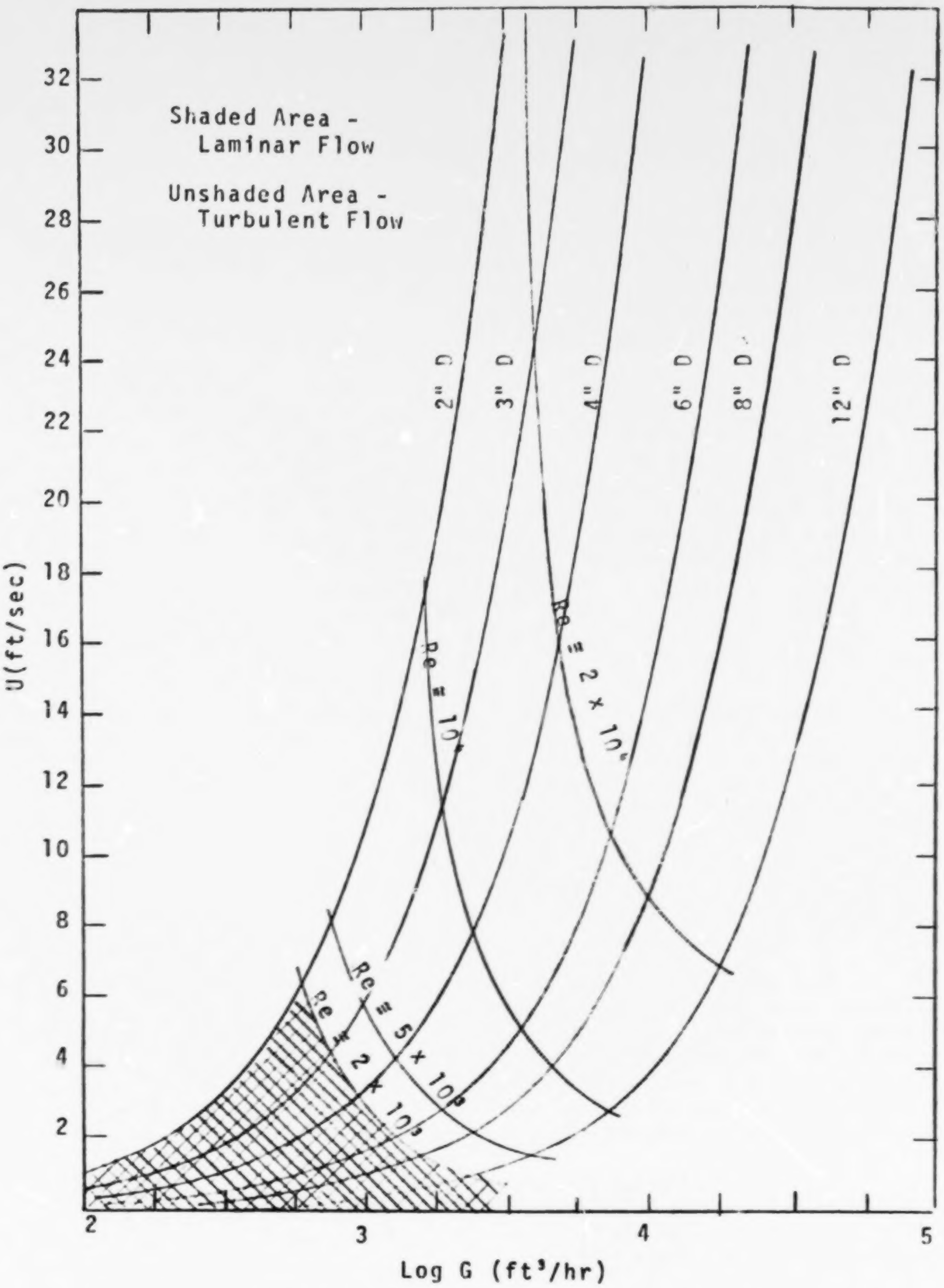


FIGURE 28 - Gas Velocity, U, Versus Log G, the Volumetric Flow Rate, for Various Diameter Ducts

TABLE XIV - COMPARISON OF CALCULATED FLUE GAS COMPOSITION FOR COAL AND NATURAL GAS COMBUSTION

Fuel	Flue Gas Composition, Volume %			
	CO_2	N_2	O_2	H_2O (from combustion)
Coal (3% S), 20% excess air	14.1	76.5	3.4	5.9
Natural Gas*				
Stiochiometric	9.7	71.6	---	18.8
10% excess air	8.9	72.2	1.7	17.2
20% excess air	8.2	72.7	3.2	15.9
30% excess air	7.6	73.1	4.5	14.8

* Based upon mass spectrometer analysis of locally available gas.

The literature on gas-liquid contacting was studied in order to obtain information on appropriate design of preliminary SO_2 scrubbing experiments, using the reaction schemes developed in Phase I. Initially, it appeared that a wetted wall column and a type of agitated horizontal pool reactor would be the most promising methods of obtaining the required information on such parameters as mass transfer coefficients, nominal retention times and efficiencies of SO_2 removal.

A review of the available data from studies of gas absorption with chemical reaction indicated that the reactive absorption of SO_2 by the candidate systems, particularly those utilizing the molten salt media, is gas film controlled. The preliminary bubbler experiments conducted in Phase I of this program indicated that, with adequate concentrations of the reactive species present, the reaction was reasonably rapid and that the exit SO_2 concentration was practically negligible.

Recent reviews of absorption processes, -- for example, Eckert (1967) -- have shown that under highly turbulent conditions, such as are produced in most packed columns, the absorption process is not readily analyzed by the diffusional film concept. Analyses of a number of systems covering a wide range in the variables affecting mass transfer (the relative volatility and the diffusion coefficient) show that the experimental values of HTU (height of a transfer unit) and HETP (height equivalent to a theoretical plate) are relatively insensitive to these variables. This was attributed to the turbulent conditions achieved at packed column pressure drops of greater than 0.5 inch H_2O per foot of column. However, because of the low pressure drop requirements necessary for flue gas processing, it is unlikely that such highly turbulent contact can be achieved for treating stack gases. The mass transfer analysis can therefore be based on the more fully developed correlations of absorption under diffusional control.

Using the empirical relationship developed by Gilliland (1934), the diffusion coefficient for SO_2 in flue gas has been estimated to be 0.73 ft^2/hr at a temperature of 300°F and a total pressure of 1 atmosphere. This value and the approximate properties of flue gas at 300°F and 1 atmosphere were used to estimate the gas film mass transfer coefficient, k_g, for several different sorption conditions.

From data on a number of studies in wetted wall columns, Sherwood (1952), suggests the best correlation to be given as:

$$\frac{k_c D}{D_v} \quad \frac{P_{BM}}{P} = 0.023 \ Re \ 0.83 \left(\frac{\mu}{\rho D_v} \right) 0.44$$

Using this correlation, the values of K_g for two flow conditions in a two-inch diameter wetted wall column were calculated at 300°F with a system pressure of 1 atmosphere and PSO_2 equal to 0.004 atmosphere. Under turbulent gas flow conditions, with a gas velocity of 10 ft/sec (Re = 5800), the gas film coefficient is approximately 0.28 lb mol/(hr)(ft^2)(atm). Although the above empirical correlation is not recommended for laminar gas flow conditions, it was felt to be of some interest to estimate the film coefficient at low gas velocity. At a gas velocity of 1 ft/sec (Re = 580), the value of K_g is of the order of 0.04 lb mol/(hr)(ft^2)(atm). This value was of interest because some of the experimental studies would be done under laminar flow conditions.

The large volumes of gas to be treated and the physical properties of the candidate scrubbing systems make the use of a horizontal channel reactor more attractive than a column reactor. Several theoretical and empirical correlations have been advanced to describe the diffusion of a gas to a planar liquid surface.

The correlation by Sherwood (1952), which proposes the concept of a "length Reynold's number", was employed in our calculations. This was based on the observation that the length of the absorbing surface is a more sifnigicant factor in mass transfer than is the cross-sectional area for gas flow. In their empirical treatment, the experimental data are correlated graphically by plotting $k_g\ P_{BM}\ (\mu/\ \rho D_v)\ 2/3/G_m$ versus Re_x. For turbulent flow conditions, at a velocity of 10 ft/sec and a surface length of 1 foot, a value for k_g of 0.25 lb mol/(hr)(ft^2) (atm) was obtained. This value corresponds quite closely to that for the two-inch wetted wall column and indicates that a horizontal channel reactor can yield results quite similar to those obtained in a wetted wall column.

For laminar flow across a plane surface, the velocity gradient across the gas stream introduces a significant effect on the rate of transfer. Byers and King (1967) give theoretical and experimental analyses of the transfer between phases in a horizontal channel of rectangular cross-section. For short duration exposures, their analysis reduces to the penetration model in which the transfer coeffieicnt is proportional to the total pressure. For longer duration exposures; i.e., residence times of the order of a few seconds, their correlation is expressed by:

$$k_{cg}\left(\frac{L}{U_oD_v}\right)^{1/2} = 0.538\left(\frac{a^2D_vL}{U_o^3}\right)^{1/6}$$

At reasonable velocity gradients, this relationship yields k_g values of the order of 0.5 lb mol/(hr)(ft^3)(atm) for an average velocity of 1 ft/sec across a plane surface one foot long. Under these same conditions, the Sherwood correlation yields a k_g value of similar magnitude.

In the correlations of film and overall transfer coefficients, the overall mass transfer coefficiant is estimated by additivity of the individual film coefficients and the proportionality constant from Henry's Law. For our candidate reaction schemes, the presence of excess reactant in the liquid phase and the stability of the reaction products make the use of Henry's Law invalid. As a first approximation, therefore, the overall mass transfer coefficient is considered to be the same as the gas film transfer coefficient.

Several conclusions relating to the design of experiments for evaluation of the candidate systems were drawn from the above analysis. The gas film coefficient and, therefore, the overall mass transfer, is significantly increased by increased gas turbulence. Experimental data on other systems also show that increased liquid turbulence will enhance the mass transfer. Because of the low pressure drop required for flue gas processing, the amount of gas phase turbulence attainable is limited. If, however, methods of liquid agitation which do not introduce significant pressure drops are employed, rapid mass transfer rates can be expected.

For preliminary studies, the use of a horizontal channel reactor without liquid agitation was expected to yield mass transfer data quite similar to that obtained with a wetted wall column. Because of the properties of the scrubbing fluids, the horizontal channel reactor introduced fewer operational problems and was preferred over a wetted wall column.

NOMENCLATURE

a = interfacial velocity gradient, hr^{-1}

D = diameter, ft

D_v = diffusion coefficient, sq ft/hr

G_m = molar gas flow rate, lb mols/(hr)(sq ft)

k_c = k_g RT = mass transfer coefficient

L = length of transfer surface, ft

P = total pressure, atm

P_{BM} = LOG MEAN DRIVING FORCE, ATM

R = gas constant, (cu ft) (atm)/(lb mol) (°R)

Re = Reynolds number, $DU \rho/\mu$

Re_x = length Reynolds number, $LU \rho/\mu$

T = absolute temperature, °R

U = gas velocity, ft/hr

U_o = interfacial velocity, ft/hr

ρ = density, lb/cu ft

μ = viscosity, lb/(hr)(ft)